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Ruthenium-catalysed copolymerization of 4-benzoylpyridine or benzophenone and 1,3-divinyltetramethyldisiloxane

Competition between formation of cyclic co-monomers and linear copolymers

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Abstract

Dihydridocarbonyl*tris* (triphenylphosphine)ruthenium (Ru)-catalysed copolymerization of 4-benzoylpyridine and 1,3-divinyltetramethyldisiloxane leads to a mixture of 2,3-benzo-6,6,8,8-tetramethyl-7-oxa-11,12-*m*-pyridino-6,8-disilacyclododecan-1-one, cyclic co-monomer (I), and copoly (2′,3-[4-benzoylpyridinylene]/3,3,5,5-tetramethyl-4-oxa-3,5-disilaheptanylene). Similarly, Ru-catalysed reaction of benzophenone and 1,3-divinyltetramethyldisiloxane leads to a mixture of 5,6,8,9-dibenzo-2,2,12,12-tetramethyl-1-oxa-2,12-disilacyclododeca-7-one, cyclic co-monomer (III) and copoly (2,2′-benzophenonylene *alt.* 2,6-benzophenonylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene). The formation of these products apparently results from the fact that only two of the four *ortho* hydrogens of 4-benzoylpyridine or benzophenone are reactive under Ru catalysis. Further, preferential reaction of one *ortho* hydrogen on each aromatic ring of 4-benzoylpyridine or benzophenone takes place. Products have been characterized by ^{1}H, ^{13}C, ^{29}Si n.m.r., i.r., u.v.-vis spectroscopy, as well as elemental analysis and/or high resolution peak matching. In addition, g.p.c., d.s.c., and t.g.a. of copolymers have been determined. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Ru, Catalyzed, Copolymerization

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1. Introduction

We have been interested in the dihydridocarbonyl*tris* (triphenylphosphine)ruthenium (Ru)-catalysed copolymerization of acetophenone and α,ω-divinylsilanes [1–3]. This polymerization reaction is related to the Ru-catalysed reaction of acetophenone with vinylsilanes which leads to monomeric *ortho* alkyl acetophenones first reported by Murai and co-workers [4,5]. This polymerization reaction involves the catalytic anti-Markovnikov addition of the *ortho* C–H bonds of acetophenone and other aryl ketones such as fluorenone [6] across the C–C double bonds of the α,ω-divinylsilane. The success of this reaction depends on the reactivity of both of the *ortho* C–H bonds of acetophenone.

There is considerable interest in polymers which contain pyridine units, either in the main chain of the polymer or as pendant groups, due to their unique properties. The pyridine nucleus provides a site which can convert the neutral polymer into an ionomer which has multiple positively charged sites either by protonation of the basic pyridine units with acids or by quaternization with alkylating agents [7]. The pyridine nuclei also provide sites for complexation with various metal cations [8]. Polysiloxanes which incorporate 4- (dialkylamino)pyridine either in the polymer backbone or as a pendant substituent have efficiently catalysed a number of reactions while showing enzyme-like substrate selectivity [9–12]. Both poly (2-vinylpyridine) and poly (4-vinylpyridine) are commercially valuable [13,14].

Likewise, benzophenone units have been incorporated into the main chain of thermally stable, commercially important engineering thermoplastic polyimide [15,16] and poly (ether/ketone) [17] materials. Covalently bonded pendant benzophenone units can absorb ultraviolet radiation and thus serve as photo-stabilizers which prevent polymer photo-degradation [18].

Attempts to apply this Ru-catalysed reaction to the copolymerization of 4-acetylpyridine and 1,3-divinyltetramethyldisiloxane failed. On the other hand, Ru-catalysed reaction between 4-benzoylpyridine and 1,3-divinyltetramethyldisiloxane gave a mixture of 2,3-benzo-6,6,8,8-tetramethyl-7-oxa-11,12-*m*-pyridino-6,8-disilacyclododecan-1-one (I) and copoly (2′,3-[4-benzoyl-pyridinylene]/3,3,5,5-tetramethyl-4-oxa-3,5-disilaheptanylene) (copoly-II). Apparently only two of the four *ortho* hydrogens, one on each aromatic

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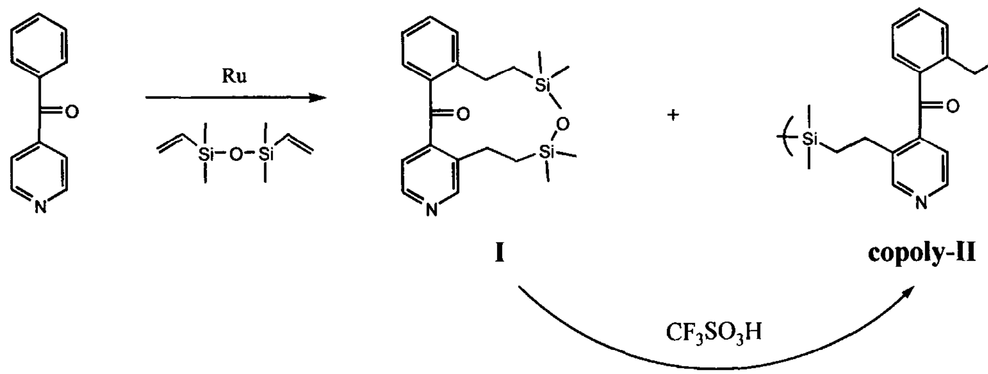

Fig. 1. Ruthenium-catalysed reaction of 4-benzoylpyridine with 1,3-divinyltetramethyldisiloxane.

ring, of 4-benzoylpyridine are reactive. Acid-assisted ring opening polymerization of cyclic co-monomer I yields copoly-II of higher molecular weight (Fig. 1).

Similar Ru-catalysed reaction of benzophenone and 1,3-divinyltetramethyldisiloxane leads to a mixture of a cyclic siloxane co-monomer, 5,6,8,9-dibenzo-2,2,12,12-tetramethyl-1-oxa-2,12-disilacyclododecan-7-one (III), and copoly (2,2′-benzophenonylene *alt.* 2,6-benzophenonylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene) (copoly-V). The fact that only two of the four *ortho* hydrogens of benzophenone react permits the synthesis of linear polymers. If, on the other hand, three or four of the *ortho* hydrogens of benzophenone had reacted, insoluble cross-linked material would have resulted [19]. Acid-catalysed ring opening polymerization of cyclic co-monomer III leads to copoly (2,2′-benzophenonylene/ 3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene) (copoly-IV) (Fig. 2).

These materials have been characterized by ^{1}H, ^{13}C, ^{29}Si n.m.r., i.r., and u.v. spectroscopy as well as by high-resolution peak matching and/or elemental analysis. Copolymers have been further characterized by g.p.c., t.g.a., and d.s.c.

2. Experimental

^{1}H and ^{13}C n.m.r. spectra were obtained on a Bruker AC-250 spectrometer operating in the Fourier transform mode. ^{29}Si n.m.r. spectra were recorded on an IBM Bruker WP-270-SY spectrometer. Five percent (w/v) chloroform-*d* solutions were used to obtain n.m.r. spectra. ^{13}C n.m.r. spectra were run with broad band decoupling. A heteronuclear gated decoupling pulse sequence (NONOE) with a 20 s delay was used to acquire ^{29}Si n.m.r. spectra [20]. These were externally referenced to TMS. Residual chloroform was used as an internal standard for ^{1}H and ^{13}C n.m.r. I.r. spectra of neat films on NaCl plates were recorded on a Perkin-Elmer Spectrum 2000 FT-i.r. spectrometer. U.v. spectra of methylene chloride solutions were acquired on a Shimadzu UV-260 ultraviolet visible spectrometer.

Gel permeation chromatography (g.p.c.) analysis of the molecular weight distribution of these polymers was performed on a Waters system. Two 7.8 × 300 mm Styragel columns packed with < 5 μm divinylbenzene cross-linked polystyrene, HR4 and HR2, in series were used for the analysis. The eluting solvent was toluene at a flow rate of

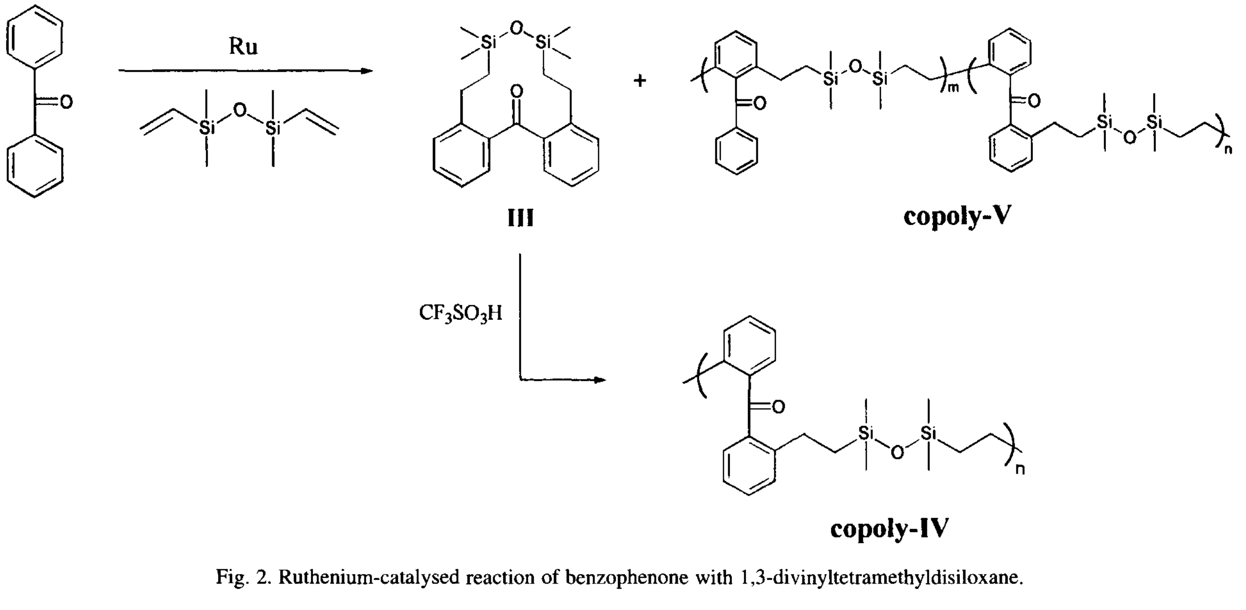

Fig. 2. Ruthenium-catalysed reaction of benzophenone with 1,3-divinyltetramethyldisiloxane.

0.3 ml/min. The retention times were calibrated against known monodisperse polystyrene standards: 929 000; 212 400; 47 500; 13 700; 794.

The glass transition temperatures (T_g) of the copolymers were determined on a Perkin-Elmer DSC-7 instrument. The mp of indium (156°C) was used to calibrate the d.s.c. The analysis program was 10°C/min from − 30 to 200°C. T.g.a. of the polymers was measured on a Shimadzu TGA-50 instrument. The temperature program was 5°C/min from 25 to 750°C. The temperature was held at 750°C for an additional 5 min.

Elemental analyses were run by Oneida Research Services Inc., (Whitesboro, NY).

All reactions were run in flame-dried glassware under argon. Dihydridocarbonyl*tris* (triphenylphosphine)ruthenium (Ru) was prepared from ruthenium trichloride hydrate [21]. 4-Benzoylpyridine and benzophenone were purchased from Aldrich and were recrystallized. 1,3-Divinyltetramethyldisiloxane and poly (hydromethylsiloxane) were purchased from Gelest. The disiloxane was distilled before use. Toluene was dried over sodium benzophenone ketyl and distilled prior to use. Triflic acid was purchased from 3M.

2.1. Preparation of copoly (2′,3-[4-benzoylpyridinylene]/ 3,3,5,5-tetramethyl-4-oxa-3,5-disilaheptanylene) (copoly-II)

Ru (0.15 g, 0.16 mmol), styrene (19 μl, 0.16 mmol), toluene (2 ml) and a Teflon-covered magnetic stirring bar were placed in an Ace pressure tube. The tube and its contents were sealed under argon, and heated at 145°C for 3 min to activate the catalyst [1]. After cooling, the tube was opened and 4-benzoylpyridine (1.00 g, 5.5 mmol) and 1,3-divinyltetramethyldisiloxane (1.02 g, 5.5 mmol) were added. The tube was resealed and the reaction mixture stirred at 150°C for 72 h. The catalyst was removed by flash column chromatography on silica gel using 90/10 hexane/ether as the eluent. The copolymer was purified by precipitation three times from THF with methanol. In this way, 1.52 g, 75% yield of copoly-II, a viscous dark brown material, $M_w/M_n = 7470/3650$, and a small amount of I were obtained. The spectral properties of copoly-II prepared in this way are virtually identical with those reported below for copoly-II prepared by triflic acid ring opening polymerization of I.

2.2. Preparation of 2,3-benzo-6,6,8,8-tetramethyl-7-oxa-11,12-m-pyridino-6,8-disilacyclo-dodecan-1-one (I)

The catalyst is activated as above using Ru (0.12 g, 0.13 mmol). 4-Benzoylpyridine (1.20 g, 6.6 mmol), 1,3-divinyltetramethyldiiloxane (1.22 g, 6.6 mmol), and toluene (22 ml) were added and the reaction mixture stirred at 135°C for 19 h. Along with I, the reaction also yields co-oligo (2′,3-[4-benzoylpyridinylene]/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene), which is terminated at one or both ends with a vinyl group attached to silicon. This material has not been fully characterized. After cooling, the contents of the tube are transferred to a round-bottomed flask equipped with a reflux condenser and a Teflon-covered magnetic stirring bar, to which was added poly (hydromethylsiloxane) (trimethylsilyl terminated, $M_w/M_n = 10\,900/4850$) (0.34 g, 0.049 mol) and 100 μl of 0.1 M H_2PtCl_6 in methanol. The flask and its contents were heated at 115°C overnight. The toluene solution was separated from a brown gelatinous mass which is insoluble in toluene. The insoluble material was washed three times with toluene. Toluene was removed from the combined fractions by evaporation under reduced pressure until 5 ml of solution remained. Ten ml of hexane was added to further precipitate any high-molecular weight material. The mixture was centrifuged and the pellet was washed three times with hexane. The hexane solutions were combined and the solvents were removed by evaporation under reduced pressure to yield 0.78 g of a mixture of I and unreacted 4-benzoylpyridine. This mixture was separated by column chromatography on a 13 × 3 cm column packed with 30 g silica gel using 60/40 hexane/ethyl acetate as the eluent. In this way, 160 mg, 6.6% yield I was obtained. ^{1}H n.m.r. δ: − 0.063 (s, 6H), − 0.058 (s, 6H), 0.67–0.74 (m, 2H), 0.91 (t, 2H, J = 12.3 Hz), 2.61–2.68 (m, 2H), 3.01 (t, 2H, J = 12.3 Hz), 7.12–7.23 (m, 3H), 7.40–7.43 (m, 2H), 8.51 (d, 1H, J = 7.6 Hz), 8.53 (s, 1H). ^{13}C n.m.r. δ: 0.39, 1.05, 18.47, 20.17, 24.13, 26.11, 121.57, 125.33, 128.73, 130.04, 130.09, 131.83, 134.02, 137.81, 144.46, 147.09, 151.13, 200.51. ^{29}Si n.m.r. δ: 7.02, 6.49. I.r. υ: 3057, 3025, 2956, 2902, 2889, 1676, 1669, 1598, 1570, 1480, 1449, 1406, 1312, 1296, 1271, 1255, 1185, 1077, 1046, 994, 939, 902, 838, 790, 778, 746, 708, 644 cm^{-1}. U.v. λ_{max} nm (ϵ): 276 (4300), 254 (9300). High resolution mass spectrometry: M^{+}. Calcd for $C_{20}H_{27}NO_2Si_2$: 369.158036. Found: 369.158400.

2.3. Preparation of copoly(2′,3-[4-benzoylpyridinylene]/ 3,3,5,5-tetramethyl-4-oxa-3,5-disila heptanylene) (copoly-II) by acid-assisted ring opening polymerization of I

To a solution of I (80 mg, 0.22 mmol) in 0.3 ml CH_2Cl_2 was added 21.5 μl (0.24 mmol) triflic acid. The mixture was stirred at 0°C for 4 h, then quenched with 200 μl hexamethyldisilazane. Two ml of CH_2Cl_2 and 2 ml of 1.8 M $NaHCO_3$ solution were added and the mixture was swirled. The CH_2Cl_2 layer was separated and the solvent removed by evaporation under reduced pressure to yield 80 mg copoly-II, $M_w/M_n = 12\,100/9450$; $T_g = -13.1$°C. ^{1}H n.m.r. δ: −0.18–0.08 (m, 12H), 0.59–0.92 (br.s, 4H), 2.44–2.64 (br.s, 2H), 2.76–2.91 (br.s, 2H), 7.07–7.42 (m, 5H), 8.49–8.52 (m, 1H), 8.55–8.59 (m, 1H). ^{13}C n.m.r. δ: −0.37, −0.25, −0.09, −0.04, −0.01, 0.03, 0.11, 0.13, 0.24, 0.28, 1.06, 1.94, 18.25, 19.95, 20.06, 20.19, 20.69, 20.76, 20.84, 24.19, 24.44, 24.49, 24.62, 26.03, 27.80, 27.94, 117.66, 122.22, 122.74, 122.90, 125.15, 125.42, 125.51, 128.81, 129.93, 130.00, 130.07, 130.24, 130.29, 130.80, 130.87, 131.99, 132.04, 132.17, 132.87, 133.03, 134.33, 134.43, 134.54, 137.08, 138.10, 139.22, 139.37, 139.64, 144.70, 145.16, 145.32, 145.50, 147.71, 148.38, 148.43, 148.64, 148.87, 149.00, 149.14, 149.39, 150.09, 150.30, 150.38, 197.02, 197.25, 199.48. ^{29}Si n.m.r. δ: 6.96, 7.31, 7.38, 7.73. I.r. ν: 3498, 3140, 3057, 2957, 2888, 1671, 1599, 1572, 1483, 1451, 1410, 1287, 1255, 1228, 1171, 1062, 1032, 943, 905, 841, 793, 705 cm^{-1}. U.v. λ_{max} nm (ϵ): 291 (3000), 255 (4200). Elemental Anal. Calc. for $C_{20}H_{27}NO_2Si_2$: C, 64.70; H, 7.38; N, 3.73. Found: C. 64.02; H, 7.42; N, 3.81.

2.4. 5,6,8,9-Dibenzo-2,2,12,12-tetramethyl-1-oxa-2,12-disilacyclododecan-7-one (III)

The catalyst was activated as above using Ru (1.78 g, 1.78 mmol). A solution of benzophenone (16.2 g, 89 mmol) and 1,3-divinyltetramethyldisiloxane (16.59 g, 89 mmol) in 200 ml of toluene was added and the reaction mixture was stirred at 135°C for 24 h. Toluene was removed by evaporation under reduced pressure. Sublimation of the crude material gave ~50% yield of III. Alternatively, III could be separated from the crude material by column chromatography. Elution with pentane/ethyl acetate (91:9) afforded III as the first to elute from the column. In this way, a 70% yield of III was obtained. ^{1}H n.m.r. δ: −0.06 (s, 12H), 0.82 (t, 4H, $J = 8$ Hz), 2.85 (t, 4H, $J = 8$ Hz), 7.17 (t, 2H, $J = 7$ Hz), 7.28 (d, 2H, $J = 7$ Hz), 7.31 (d, 2H, $J = 7$ Hz), 7.38 (t, 2H, $J = 8$ Hz). ^{13}C n.m.r. δ: 0.82, 19.45, 26.46, 125.25, 129.22, 129.56, 130.73, 140.08, 143.59, 202.94. ^{29}Si n.m.r. δ: 6.74. I.r. ν: 3064, 2954, 1665, 1598, 1570, 1481, 1449, 1411, 1297, 1252, 1179, 1064 (br), 932, 841, 784 cm^{-1}. U.v. λ_{max} nm (ϵ): 250 (4000), 288 (2850), 337 (108). Elemental Anal. Calc. for $C_{21}H_{28}Si_2O_2$: C, 68.48; H, 7.61. Found: 68.73; H, 7.51.

2.5. Copoly(2,2′-benzophenonylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene) (copoly-IV) by acid-catalysed ring opening polymerization of III

A solution of 5,6,8,9-dibenzo-2,2,12,12-tetramethyl-1-oxa-2,12-disilacyclododecan-7-one (III) (250 mg, 0.68 mmol) in 1.25 ml of CH_2Cl_2 was added to a 10 ml round-bottomed flask equipped with a Teflon-covered magnetic stirring bar and a reflux condenser. The solution was stirred at 0°C for 1 h. At that time, 1.2 μl of freshly distilled triflic acid was added. The solution was stirred at 0°C for 10 h. The reaction was quenched by addition of 2 μl hexamethyldisilazane. ^{1}H n.m.r. δ: − 0.02 (s, 12H), 0.82 (m, 4H), 2.73 (m, 4H), 7.10 (t, 2H, $J = 7$ Hz), 7.22 (d, 2H, $J = 9$ Hz), 7.25 (d, 2H, $J = 7$ Hz), 7.34 (t, 2H, $J = 8$ Hz). ^{13}C n.m.r. δ: 0.91, 21.60, 28.02, 125.83, 130.60, 131.20, 131.83, 139.21, 146.35, 201.30. ^{29}Si n.m.r. δ: 7.28. I.r. ν: 3064, 3018, 2955, 2930, 2886, 1664, 1598, 1571, 1481, 1447, 1409, 1296, 1253, 1178, 1057 (br), 994, 935, 842, 782, 763, 727, 641 cm^{-1}. U.v. λ_{max} nm (ϵ): 250 (3930), 287 (2900), 339 (124). $M_w/M_n = 19\,400/13\,550$. $T_g = 0.6$°C. Elemental Anal. Calc. for $C_{21}H_{28}Si_2O_2$: C, 68.48; H, 7.61. Found: C, 67.83; H, 7.51.

2.6. Copoly(2,2′-benzophenonylene alt. 2,6-benzophenonylene-1,3-phenylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene) (copoly-V)

The catalyst was activated as above using Ru (140 mg, 0.153 mmol). Benzophenone (1.955 g, 10.7 mmol) and 1,3-divinyltetramethyldisiloxane (2 g, 10.7 mmol) were added. The tube was purged with argon, capped and heated at 135°C for 24 h. The crude polymer was dissolved in methylene chloride and precipitated by addition of methanol three times. In this way, 1.9 g, 48% yield of copoly-V was obtained. ^{1}H n.m.r. δ: −0.12 (s, 1.2H), −0.08 (s, 1.9H), −0.06 (s, 1.9H), −0.05 (s, 1.4H), 0.01 (s, 3.8H), 0.07 (s, 1H), 0.14 (s, 0.7H), 0.74–0.88 (m, 4H), 2.32–2.39 (m, 1.5H), 2.73–2.79 (m, 2.5H), 7.05–7.15 (m, 2H), 7.23–7.40 (m, 5.5H), 7.77 (d, 0.5H, $J = 7.5$ Hz). ^{13}C n.m.r. δ: 0.17, 0.52, 20.35, 20.77, 20.85, 21.61, 25.51, 26.75, 26.93, 27.28, 28.56, 124.95, 125.07, 125.83, 128.30, 129.33, 129.83, 129.97, 130.17, 130.42, 131.04, 133.00, 138.42, 141.38, 145.56, 198.54, 200.44, 201.57, 202.84. ^{29}Si n.m.r. δ: 5.82 (s, 0.16Si), 5.94 (s, 0.04Si), 6.65 (s, 0.12Si), 6.88 (s, 0.08Si), 7.00 (s, 0.24Si), 7.02 (s, 0.22Si), 7.10 (s, 0.08Si), 7.16 (s, 0.10Si), 7.28 (s, 0.67Si), 7.35 (s, 0.18Si), 7.68 (s, 0.10Si). I.r. ν: 3059, 3014, 2954, 2929, 2885, 1665, 1594, 1572, 1477, 1449, 1410, 1292, 1254, 1176, 1060 (br), 994, 933, 841, 787, 763, 705, 640 cm^{-1}. U.v. λ_{max} nm (ϵ): 251 (4100), 288 (2920), 342 (194). $M_w/M_n = 10\,320/7770$. $T_g = -26$°C.

3. Results and discussion

The failure of 4-acetylpyridine to undergo Ru-catalysed copolymerization with 1,3-divinyltetramethyldisiloxane under conditions which are successful with acetophenone and 1,3-divinyltetramethyldisiloxane may be due to the decreased reactivity of the *ortho* C–H bonds of pyridine toward Ru activation compared to those of benzene. This may be related to difficulty in carrying out aromatic electrophilic substitution reactions on pyridine nuclei. Alternatively, since activation of the *ortho* C–H bonds depends upon coordination of the unsaturated Ru centre by the oxygen of the carbonyl group [4,5], this lack of reactivity of 4-acetylpyridine may reflect competitive coordination of the Ru centre by the pyridine nitrogen.

Nevertheless, the Ru-catalysed reaction of 4-benzoylpyridine and 1,3-divinyltetramethyldisiloxane is successful and yields a mixture of copoly-II and cyclic co-monomer I. Low concentration favours the formation of I. The formation of cyclic monomers and linear polymers have been observed in both acid- and base-catalysed polymerization of cyclic siloxanes [22–24]. Preparation of I under dilute conditions also yields co-oligo(2′,3-[4- benzoylpyridinylene]/3,3,5,5-tetramethyl-4-oxa-3,5- disila-1,7-heptanylene) which is terminated at one or both ends with a vinyl group attached to silicon. Attempts to separate I and the co-oligomer by a variety of conventional methods failed. Removal of these vinyl-terminated co-oligomers was achieved by covalently bonding them to poly(hydromethylsiloxane) via a Pt-catalysed hydrosilylation reaction.

Based on the lack of reactivity of 4-acetylpyridine, one might anticipate that the structure of the copolymer would be copoly (1-[4′-pyridinoyl]2,6-phenylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene) in which both the *ortho* C–H bonds of the benzene ring, but neither of the *ortho* C–H bonds of the pyridine react. In fact, in cyclic co-monomer I, the 4-benzoylpyridine unit is incorporated by reaction of one of the *ortho* C–H bonds of the benzene ring and one of the *ortho* C–H bonds of the pyridine ring. Both the methylene groups adjacent to aromatic ring and those next to silicon can be distinguished by ^{1}H n.m.r. The methylene group adjacent to the pyridine ring comes at 3.01 ppm, whereas the methylene group adjacent to the benzene ring is found as a multiplet centred at 2.65 ppm. The methylene group adjacent to the silicon which is closest to the pyridine ring is found at 0.91 ppm. Finally, the methylene adjacent to the silicon atom which is closest to the benzene ring is found as a multiplet which is centred at 0.70 ppm.

Similarly in copoly-II, at least 90% of the 4-benzoylpyridine units are incorporated by reaction of one *ortho* C–H of the benzene ring and one *ortho* C–H of the pyridine ring, i.e., as 2′,3-(4-benzoylpyridinylene) units. As expected, two types of benzylic methylene groups are observed in the ^{1}H n.m.r. spectra. A broad singlet centred at 2.83 ppm is assigned to methylene groups adjacent to the pyridine rings, whereas a broad singlet centred at 2.54 ppm is assigned to methylene groups bonded to the benzene rings. The singlet at 2.83 ppm is about 10% smaller than the one at 2.54 ppm. This can be accounted for if, in copoly-II, about 10% of the 4-benzoylpyridine units are incorporated as 1-(4′-pyridinoyl)-2,6-phenylene units. A broad singlet at 2.3 ppm whose area is equal to $\sim$10% may be assigned to methylene units of this type. The methylene groups adjacent to silicon, a broad singlet centred at 0.75 ppm, are not differentiated in copoly-II.

Attempts to carry out catalytic acid-accelerated ring opening polymerization of I failed. This may be due to protonation of the pyridine nitrogen, rather than the oxygen of the disiloxane unit which is essential for ring opening. On the other hand, acid-accelerated ring opening polymerization of I has been achieved by use of a slightly greater than stoichiometric amount of triflic acid. The polymer thus obtained has a higher molecular weight than that obtained by direct Ru-catalysed copolymerization and is perfectly regular in its incorporation of 4-benzoylpyridine units.

Ru-catalysed reaction of benzophenone and 1,3-divinyltetramethyldisiloxane has been shown to yield a mixture of cyclic co-monomer and irregular copolymer in which 2,2′-benzophenoylene units are favoured over the

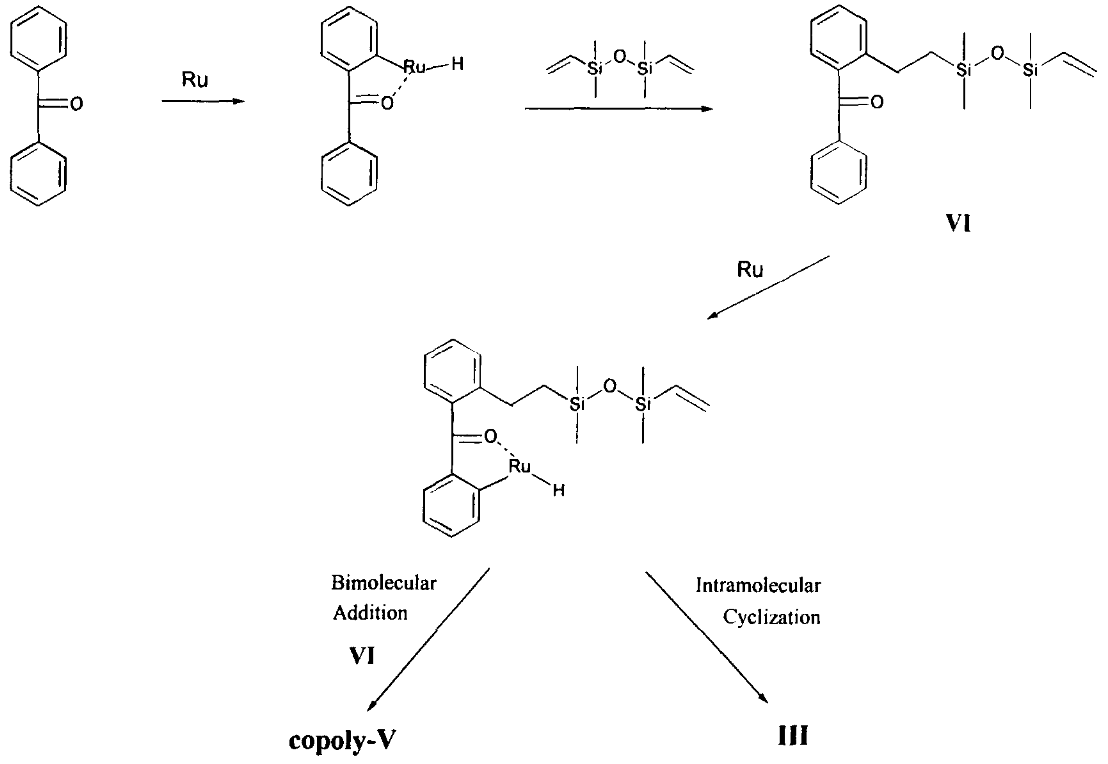

Fig. 3. Possible mechanism for the ruthenium-catalysed reaction of benzophenone with 1,3-divinyltetramethyldisiloxane.

2,6-benzophenonylene units by a ratio of ~3:1. The formation of these products apparently results from the fact that only two of four *ortho* hydrogens of benzophenone are reactive.

1-[2′-Benzoylphenethyl]-3-vinyltetramethyldisiloxane (VI), formed by Ru-catalysed reaction of benzophenone and 1,3-divinyltetramethyldisiloxane, is probably an important intermediate product in these reactions. VI may be formed by initial insertion of a coordinately unsaturated Ru catalyst species into an activated *ortho* C–H bond of benzophenone to give an aryl–Ru–H species which reacts further with the C–C double bond of 1,3-divinyltetramethyldisiloxane to yield VI. III may be formed by insertion of a coordinately unsaturated Ru species into an *ortho* C–H bond of the unsubstituted aryl ring of VI to yield a reactive aryl–Ru–H species which preferential undergoes intramolecular reaction with the terminal C–C double bond. On the other hand, bimolecular reaction of VI with a molecule of ruthenium activated VI begins the process of polymer formation. The ratio of cyclic co-monomer III to irregular copoly-V was strongly dependent on the concentration at which the Ru-catalysed reaction was conducted. Lower concentration favours the cyclic co-monomer III (Fig. 3).

In the polymerization process, reaction of an *ortho* C–H bond of an unsubstituted aromatic ring with the Ru catalyst is favoured over reaction at an *ortho* C–H bond of an aromatic ring which is already mono substituted. ^{1}H n.m.r. permits analysis of the structure of these polymers. The benzylic hydrogens are particularly sensitive to the presence or absence of a second substituent on the same aromatic ring. The benzylic hydrogens of 2,2′-benzophenonylene group are found at ~2.73 ppm, whereas those associated with 2,6-benzophenonylene groups are found at ~2.35 ppm. By comparison, the methylene groups adjacent to Si are both observed at ~0.82 ppm.

The formation of cyclic monomers and linear polymers have been observed in numerous types of polymerization reactions. For example, in both acid- and base-catalysed polymerization of monomeric cyclic siloxanes, an equilibrium mixture of cyclic monomers and linear polymers is often found [22–24]. Triflic acid-catalysed polymerization of cyclic monomer III leads to a completely regular copoly-IV (Fig. 2).

While the molecular weight of regular copoly-IV M_w/M_n = 19 400/13 600 is approximately twice that of irregular copoly-V M_w/M_n = 10 300/7800, both are probably sufficiently high to permit meaningful comparison of their properties. The thermal stabilities of both are quite similar. Both copoly-IV and copoly-V lose a few percent of their initial sample weight between 100 and 350°C. Between 350 and 400°C less than 10% weight loss is observed. Above 400°C more rapid, catastrophic weight loss occurs. By 450°C, 15% of the sample weight for copoly-V remains, while less than 10% of the weight of copoly-IV is present. By comparison, copoly-II is less thermally stable and it undergoes a two-stage thermal decomposition. Copoly-II was stable to 200°C. Between 200 and 300°C, a 25% weight loss is observed. Above 300°C, more rapid weight loss occurs, such that by 500°C only 10% of the initial sample weight remains. Above

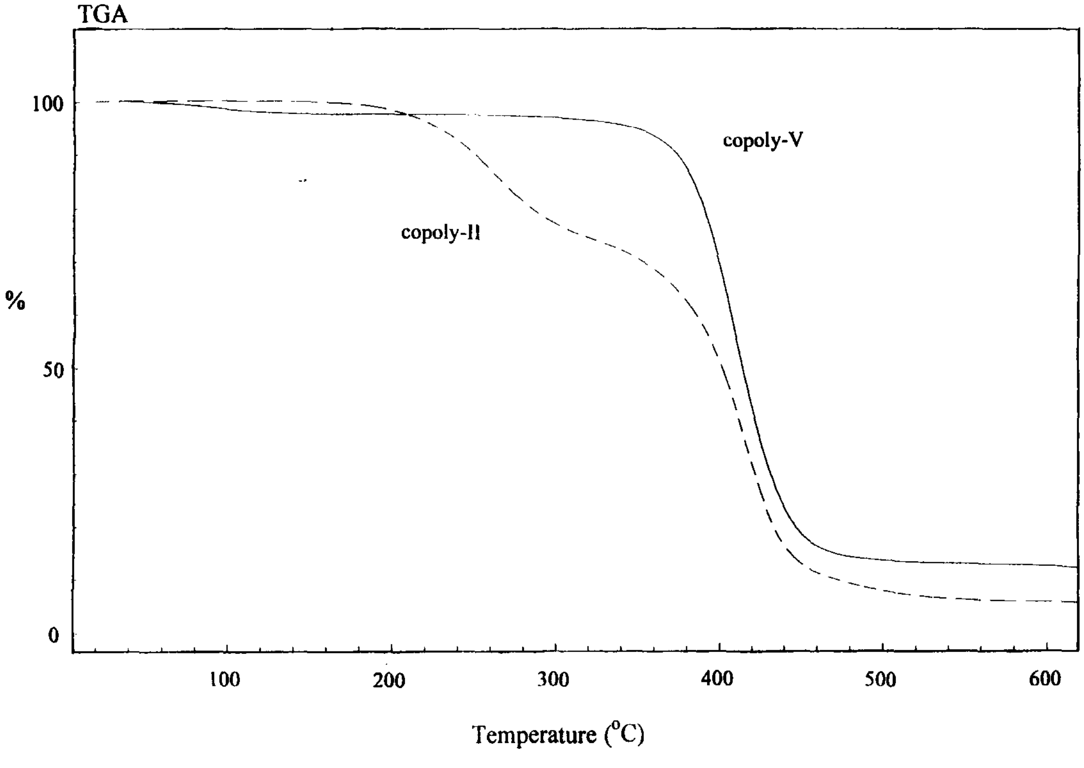

Fig. 4. Comparison of the thermal stability of copoly-II and copoly-V by thermogravimetric analysis.

this temperature a very slow further weight loss occurs (Fig. 4).

The T_g of the regular copoly-IV is significantly higher (0.6°C) than the T_g of the irregular copoly-V (−26°C). This difference is reasonable since mixtures are well known to depress T_g. The T_g of copoly-II is intermediate in value at −13°C.

4. Conclusions

For both benzophenone and 4-benzoylpyridine only two of their four *ortho* hydrogens are reactive to Ru-catalysed copolymerization with 1,3-divinyltetramethyldisiloxane. This permits the formation of linear polymers. Further, the formation of cyclic co-monomers is competitive with the formation of linear polymers for both benzophenone and 4-benzoylpyridine. This is the first observation of the formation of cyclic co-monomers in Ru-catalysed step-growth copolymerization reactions.

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