

Synthesis and characterization of novel crown ether containing copolymers Ru catalyzed copolymerization of 4'-acetylbenzocrown ethers with α,ω -dienes

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Summary

Ruthenium catalyzed step growth copolymerization of 4'-acetylbenzo-15-crown-5 and 4'-acetylbenzo-18-crown-6 and α,ω -dienes such as 1,3-divinyltetramethyldisiloxane or 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene give novel copolymers which incorporate crown ethers into the polymer backbone in a regular manner. The synthesis of these thermally stable copolymers and their characterization is reported. Lithium cation crown complexes have been formed.

Introduction

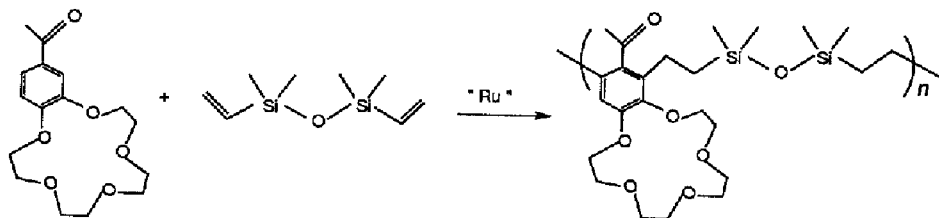
Crown ethers have the ability to complex cations by chelation and thus facilitate the solution of many insoluble ionic substances in nonpolar aprotic solvents. Separation of the cation and the anion, facilitated by crown ether complexation of the cation, often increases the reactivity of the anion and thus catalyzes numerous chemical reactions. Macrocyclic crown ethers have been incorporated into polymeric structures either as part of the backbone or anchored to it as pendant ligands. Polymeric crown ethers have been utilized as phase transfer catalysts. Further, polymeric crown ether cation complexes are novel polyelectrolytes (1-3).

Synthetically crown ethers have been frequently incorporated into polymer backbones by condensation type polymerizations. The first example of a polymeric crown ether was prepared by reaction of isophthaloyl chloride with 4,4'-diaminodibenzo-18-crown-6 (4). Polymers substituted with pendant crown ether groups have been prepared by a number of methods. Among these are the polymerization of vinyl derivatives of benzo crown ethers, (5) Williamson ether synthesis between, for example, hydroxymethyl substituted benzo crown ethers and poly(4-bromobutylmethylsiloxanes) (6) as well as by platinum catalyzed hydrosilation reactions between poly(methylsiloxane) and crown ethers containing pendant terminal alkene groups (7).

In this paper, we should like to report the dihydridocarbonyl\alpha,\omega-dienes such as 1,3-divinyltetramethyldisiloxane and 3,3,6,6-hexamethyl-3,6-disila-1,7-octadiene to yield novel polymers which incorporate crown ethers in the polymer chain. This type of reaction was first reported in monomer systems by Murai, who described the Ru catalyzed addition of the *ortho* C-H bonds of acetophenone across the C-C double bonds of olefins such as trimethylvinylsilane to yield *ortho*-alkyl substituted acetophenones (8-10). We have previously shown that this reaction can

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be applied to achieve step-growth copolymerization of aromatic ketones and α,ω -dienes (11-16). In this paper we report the use of this procedure to prepare the first polycarbosilanes in which a crown ether is incorporated into the polymer backbone in a regular manner.



Experimental:

^1H and ^{13}C NMR spectra were obtained either on a Bruker AC-250 or an AM-360 spectrometer operating in the Fourier Transform mode. ^{29}Si NMR were recorded on an IBM-Bruker WP-270-SY spectrometer. Five percent w/v solutions in chloroform-*d* were used to obtain NMR spectra. ^{13}C NMR spectra were run with broad band proton decoupling. ^{29}Si NMR spectra, referenced to TMS, were obtained using gated decoupling pulse sequence (NONOE) with a 20 sec delay (17). 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.

GPC analysis of the molecular weight distribution of the copolymers 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 $< 10\ \mu\text{m}$ particles of monodisperse crosslinked styrene divinyl benzene copolymer were used: 1×10^4 (Waters Ultrastaygel), 1×10^3 (Waters Ultrastaygel) and 500 Å (Polymer Laboratories PL_{gel}). HPLC grade THF was used as the eluting solvent at a flow rate of 1 mL/min. The retention times were calibrated against those of known monodisperse polystyrene standards: M_w 612,000; 114,200; 47,500; 18,700; 5,120; 2,200 whose M_w/M_n are less than 1.09.

TGA analysis 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 T_g s of the copolymers were determined by DSC on a Perkin-Elmer DSC-7 instrument. The melting points of indium (156°C) and water (0°C) were used to calibrate the DSC. The program for the analysis was -70°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, Whitesboro, NY.

All reactions were conducted in flame dried equipment under argon. 1,3-Divinyl-tetramethyldisiloxane and 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene were obtained from United Chemical Technologies. Dihydridocarbonyl

Copolymerization Procedure: in a 25 mL two neck round bottom flask equipped with a reflux condenser, a rubber septum, and a Teflon covered magnetic stirring bar was placed Ru (48 mg, 0.05 mmol), and toluene 0.4 mL. The flask and its contents were heated till the

solvent refluxed. At this time, styrene (5.8 μL , 5.2 mg, 0.05 mmol) was added via a syringe. The color of the reaction mixture immediately turned to black. After two minutes, a mixture of 4'-acetylbenzo-15-crown-5 (0.31 g, 1 mmol) and 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene (0.20 g, 12 mmol) dissolved in toluene 0.5 mL was added by injection. The reaction mixture was heated to reflux for 36 h. Volatiles were removed by evaporation under reduced pressure. The crude polymer was purified by precipitation three times from a mixture of THF and pentane. In this way, 0.42 g, 82% yield of pure copolymer $M_w/M_n = 14560/8920$, $T_g = 23^\circ\text{C}$ was obtained.

Copoly[2-acetyl-4,5-(15-crown-5)-1,3-phenylene/3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene] (I). ^1H NMR δ : -0.05(s, 12H), 0.36(s, 4H), 0.72-0.78(br.m, 4H), 2.33-2.40 (br.m, 4H), 2.40(s, 3H), 3.68(s, 8H), 3.87-3.92(br.m, 4H), 4.08(s, 4H), 6.53(s, 1H). ^{13}C NMR δ : -4.22, 6.92, 17.32, 17.43, 22.18, 27.28, 33.32, 67.69, 69.37, 70.01, 70.23, 70.36, 70.76, 70.96, 72.62, 110.58, 134.11, 134.60, 135.83, 143.87, 151.82, 207.38. ^{29}Si NMR δ : 4.09, 4.11. IR ν : 2951, 2876, 1695, 1592, 1482, 1454, 1417, 1310, 1249, 1169, 1133, 1084, 1054, 993, 911, 832, 735 cm^{-1} . UV: 285-267 nm, λ_{max} (ϵ): 273 (840), 228 (4800). Elemental Anal. Calcd. for $\text{C}_{26}\text{H}_{40}\text{O}_6\text{Si}_2$: C, 61.37; H, 8.65. Found: C, 59.75; H, 8.18.

Copoly[2-acetyl-4,5-(15-crown-5)-1,3-phenylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene] (II) was prepared as above by reaction of 4'-acetylbenzo-15-crown-5 (0.47 g, 1.5 mmol) and 1,3-divinyltetramethyldisiloxane (0.29 g, 1.5 mmol). In this way, 0.42 g, 55% yield of pure copolymer $M_w/M_n = 8500/5000$, $T_g = 20^\circ\text{C}$ was obtained. ^1H NMR δ : 0.06(s, 12H), 0.75-0.80(br.m, 4H), 2.41-2.49(br.m, 4H), 2.49(s, 3H), 3.70(s, 8H), 3.87-3.93(br.m, 4H), 4.00(s, 4H), 6.55(s, 1H). ^{13}C NMR δ : 0.11, 0.22, 20.73, 20.88, 21.63, 26.65, 33.34, 67.72, 69.39, 70.05, 70.27, 70.35, 70.78, 70.97, 72.63, 110.68, 134.20, 134.32, 135.62, 143.98, 151.85, 207.39. ^{29}Si NMR δ : 7.02, 7.65. IR ν : 2955, 2869, 1946, 1695, 1592, 1483, 1454, 1439, 1415, 1352, 1308, 1255, 1131, 1061, 923, 841, 798, 722 cm^{-1} . UV 275-260 nm, λ_{max} (ϵ) 265(3022), 228 (11,000). Elemental Anal. Calcd for $\text{C}_{24}\text{H}_{40}\text{O}_7\text{Si}_2$: C, 57.99; H, 8.10. Found: C, 57.29; H, 7.88.

Copoly[2-acetyl-4,5-(18-crown-6)-1,3-phenylene/3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene] (III) was prepared by reaction of 4'-acetylbenzo-18-crown-6 (0.28 g, 0.8 mmol) and 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene (0.16 g, 0.8 mmol). In this way, 0.34 g, 79% yield of pure copolymer III, $M_w/M_n = 12,000/9,000$, $T_g = 9^\circ\text{C}$ was obtained. ^1H NMR δ : 0.04(s, 6H), 0.06(s, 6H), 0.46(s, 4H), 0.82-0.87(br.m, 4H), 2.39-2.48(br.m, 4H), 2.48(s, 3H), 3.71(s, 8H), 3.78(s, 4H), 3.91-3.98(br.m, 4H), 4.19-4.23(br.m, 4H), 6.65(s, 1H). ^{13}C NMR δ : -4.60, 6.88, 17.03, 17.13, 22.18, 26.73, 33.48, 68.04, 69.63, 70.26, 70.31, 70.50, 70.60, 70.64, 70.72, 71.04, 72.06, 111.01, 134.61, 134.80, 135.96, 143.52, 151.70, 207.29. ^{29}Si NMR δ : 4.21, 4.24. IR ν : 3012, 2884, 1716, 1618, 1508, 1466, 1431, 1379, 1343, 1324, 1273, 1202, 1160, 1095, 1068, 1005, 967, 874, 791, 751 cm^{-1} . UV λ_{max} (ϵ) 303 (800), 272(2250), 228(8564). Elemental Anal. Calcd. $\text{C}_{28}\text{H}_{48}\text{O}_7\text{Si}_2$: C, 60.83; H, 8.68. Found: C, 60.16; H, 8.49.

Copoly[2-acetyl-4,5-(18-crown-6)-1,3-phenylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene] (IV) was obtained by the reaction of 4'-acetylbenzo-18-crown-6 (0.53 g, 1.5 mmol) and 1,3-divinyltetramethyldisiloxane (0.28 g, 1.5 mmol) as above. In this way, 0.56 g, 65% yield of pure copolymer IV $M_w/M_n = 9,600/7,500$, $T_g = -3^\circ\text{C}$ was obtained. ^1H NMR δ : 0.86-0.11(br.s, 12H), 0.79-0.82(br.m, 4H), 2.43(s, 3H), 2.43-2.49(br.m, 4H), 3.65(br.s, 8H), 3.71(br.s, 4H), 3.84-3.90(br.m, 4H), 4.13-4.15(br.s, 4H), 6.59(s, 1H). ^{13}C NMR δ : 0.16, 20.78, 21.56, 26.53, 33.24, 68.10, 68.57, 69.29, 69.63, 69.86, 70.26, 70.42, 70.60, 70.95, 72.01, 111.25, 134.20, 134.35, 135.41, 143.79, 151.62, 207.16. ^{29}Si NMR δ : 6.97, 7.12. IR ν : 2952, 2876, 1695, 1592, 1567, 1514, 1483, 1453, 1416, 1351,

1307, 1253, 1207, 1130, 1057, 952, 897, 841, 797 cm^{-1} . UV λ_{max} (ϵ) 304(657), 273(1840), 227 (6800). Elemental Anal. Calcd for $\text{C}_{26}\text{H}_{44}\text{O}_3\text{Si}_2$: C, 57.74; H, 8.14. Found: C, 56.98; H, 7.68.

Results and Discussion:

Polycarbosilanes and polysiloxanes containing benzocrown ethers in the backbone have been synthesized by a Ru catalyzed copolymerization between 4'-acetylbenzocrowns and α,ω -dienes such as 1,3-divinyltetramethyldisiloxane and 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene. Polycarbosilanes with pendant crown ether groups have been previously prepared by the anionic ring opening polymerization of a crown ether substituted 1-silacyclopent-3-ene (21). Complex formation between the 15-crown-5 units in the polymers and lithium cations has been studied by ^{13}C NMR spectroscopy. While it is not possible to assign the ^{13}C resonances observed for the oxyethylene units to specific carbons, it is apparent that these signals are significantly shifted when 1 equivalent of lithium perchlorate is added for each 15-crown-5 unit. On the other hand, the ^{13}C resonances due to the other carbons are shifted much less (See data below).

^{13}C NMR of I in acetonitrile- d_3 , δ : -3.85, 7.40, 7.49, 17.98, 18.30, 22.79, 28.06, 33.91, 68.57, 69.75, 70.49, 70.63, 71.11, 71.22, 71.53, 73.31, 111.95, 135.10, 135.24, 136.90, 144.66, 152.62, 207.63.

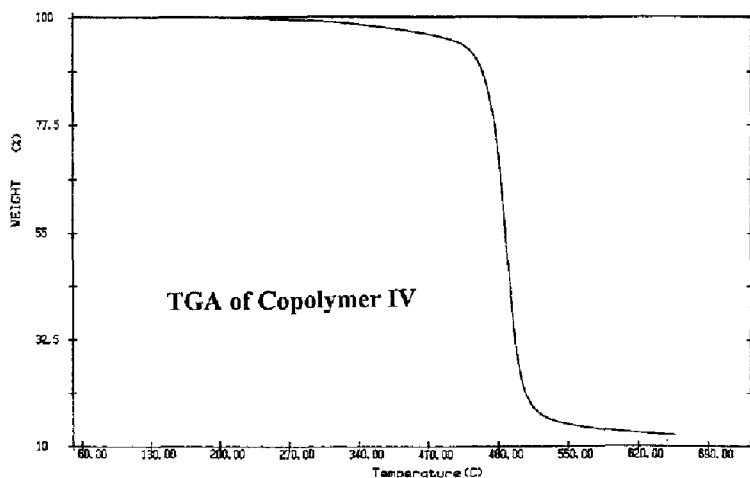
^{13}C NMR of LiClO_4 complex of I in acetonitrile- d_3 , δ : -4.70, -4.57, 6.40, 6.61, 17.14, 17.45, 21.62, 27.32, 33.18, 65.40, 66.31, 66.63, 66.87, 67.74, 69.10, 69.78, 71.65, 110.76, 135.08, 137.97, 141.54, 150.31, 207.76.

^{13}C NMR of II in acetonitrile- d_3 , δ : 0.48, 21.54, 21.72, 22.35, 27.41, 33.97, 68.59, 69.80, 70.05, 70.53, 71.11, 71.28, 71.55, 73.35, 111.96, 134.99, 135.16, 136.57, 144.75, 152.66, 207.80.

^{13}C NMR of LiClO_4 complex of II in acetonitrile- d_3 , δ : -0.96, -0.81, 19.16, 21.18, 24.97, 27.08, 32.53, 65.87, 66.76, 67.34, 68.21, 68.79, 69.55, 69.74, 72.24, 109.89, 135.20, 135.73, 138.00, 142.10, 150.74, 207.69.

Thermal Stability

These polymers are quite thermally stable. For example, IV is thermally stable to 270°C. Between 270 and 465°C a seven percent linear weight loss occurs. Above 465°C rapid weight loss is observed. By 515°C only fifteen percent of the initial sample weight remains (See Figure). Copolymers I, II and III have similar thermal stabilities.



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References:

1. Moore JA, Partain EM III (1984) Ion Binding Polyesters and Polyamides Containing THF Rings In: Mathias LJ, Carraher CE Jr (eds) Crown Ethers and Phase Transfer Catalysis in Polymer Science. Plenum Press, New York (pp 291-328).
2. Smid J, Sinta R (1984) Ion Binding Properties of Network Polymers with Pendant Crown Ether Ligands, *ibid* (pp 329-344).
3. Yagi K, Sanchez MC (1984) Selective Cation Binding by Polymers with Pendant Crown Ethers, *ibid* (pp 345-358).
4. Feigenbaum W. M, Michel RH, *J Polym Sci* (1971) A-1, 9: 817.
5. Kopolow S, Hogen-Esch TE, Smid J (1973) *Macromolecules* 6:133.
6. Wienk MM, Stolwijk TB, Sudholter EJR, Reinhoudt DN, *J Am Chem Soc* (1990)112: 797.
7. Abed-Ali SS, Brisdon BJ, England R (1989) *Macromolecules* 22:3969.
8. Murai S, Kakiuchi F, Sekine S, Tanaka Y, Sonoda M, Chatani N (1993)*Nature* 336:529
9. Murai S, Kakiuchi F, Sekine S, Tanaka Y, Kamatani A, Sonoda M, Chatani N (1994) *Pure & Applied Chem* 66:1527.
10. Kakiuchi F, Sekine S, Tanaka Y, Kamatani A, Sonoda M, Chatani M, Murai S (1995) *Bull Chem Soc Jpn* 68:62.
11. Guo H, Weber WP (1994) *Polymer Bull* 32:525.
12. Guo H, Tapsak MA, Weber WP (1995) *Polymer Bull* 34:49.
13. Guo H, Tapsak MA, Weber WP (1995) *Polymer Preprints* 36-1:705.
14. Guo H, Wang G, Tapsak MA, Weber WP (1995) *Macromolecules* 28:5686.
15. Guo H, Weber WP (1995) *Polymer Bull* 35:259.
16. Guo H, Tapsak MA, Weber WP (1995) *Macromolecules* 28:4714.
17. Freeman R, Hill HDW, Kaptein R (1972) *J Magn Reson* 7:327.
18. Levison JJ, Robinson SD (1970) *J Chem Soc A*:2947.
19. Wada F, Matsuda T (1980) *Bull Chem Soc Jpn* 53:421.
20. Talma AG, van Vossen H, Sudholter EJR, van Eerden J, Reinhoudt, DN, Syn (1986) 680.
21. Wang L, Weber WP (1993) *Macromolecules* 26:969.