Synthesis of Carbosilane Monomers and Polymers with Mesogenic Pendant Groups. Preparation and Characterization of Aryloxy-Substituted Poly(1-sila-*cis*-pent-3-enes)

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ABSTRACT: The synthesis and anionic ring-opening polymerization of 1-(3′-(aryloxy)propyl)-1-silacyclopent-3-ene monomers are described. These monomers were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR, IR and UV/vis spectroscopy, GC/MS, high-resolution MS, and elemental analysis. After polymerization and purification, the polymers were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR, IR and UV/vis spectroscopy, GPC, TGA, DSC, and elemental analysis. The occurrence of liquid crystalline behavior in two of these systems was detected by DSC. A smectic phase is suggested for poly[1-methyl-1-(3′-phenoxypropyl)-1-sila-*cis*-pent-3-ene] by polarizing optical microscopy. The T_gs of the polymers are found to be linearly dependent upon the length of the pendant 3′-(aryloxy)propyl group, whereas the thermal stability of the polymers is not. An alternative method to prepare these materials based on hydrosilation graft techniques is described.

Introduction

Liquid crystalline materials demonstrate unusual phase behavior which combines properties of the homogeneous liquid and the ordered crystalline states.[1,2] Polymeric side chain[3–5] liquid crystalline materials comprised of a highly flexible, low-T_g siloxane backbone in which the silyl centers are substituted with pendant aryl or aryloxy groups have been prepared.[3,6] These materials represent an important class of side chain liquid crystalline polymers because of their many desirable properties. However, the siloxane backbone is susceptible to hydrolysis under acidic or basic catalysis as well as to thermal or base-catalyzed redistribution to cyclics.[7] This may limit the overall utility of such materials.

The relatively low T_gs observed for poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (−64 °C) and poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) (−16 °C)[8] suggest that materials based on stereoregular unsaturated carbosilane backbones substituted with pendant aryloxy groups might exhibit liquid crystalline behavior at room temperature. Such materials would represent a novel class of liquid crystalline substances. These materials might be expected to have better high temperature and hydrolytic stability than siloxane materials.

The preparation of these polymers could be accomplished in two ways, as illustrated in Scheme I. The more traditional method would be to prepare a reactive polymer with Si–H groups. This then would be coupled, by a graft hydrosilation reaction, to an olefinic group bearing the desired pendant mesogenic moiety. This approach has often been utilized to prepare liquid crystalline materials via the hydrosilation reaction between poly(methylsiloxanes) and allyl-substituted mesogens.[6,9] An alternative method would be to prepare the monomer with the desired pendant group and then polymerize it. This method is superior if no cross-linking or side products are obtained due to the guarantee of 100% substitution of the desired pendant group within the polymer system. This paper describes initial investigations into both synthetic chemistries and the study of the liquid crystalline properties of some examples of this novel class of materials.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-250 spectrometer operating in the Fourier transform mode and are referenced to residual solvent peaks. ^{13}C NMR spectra were obtained with broad-band proton decoupling. ^{29}Si NMR spectra were recorded on a Bruker SY-270 spectrometer by using the heteronuclear gated decoupling pulse sequence (NONOE) with a pulse delay of 30 s.[10] Ten percent weight/volume solutions in chloroform-*d* were used to measure ^{1}H and ^{13}C NMR spectra, whereas 20% solutions were utilized to obtain ^{29}Si NMR spectra.

IR spectra were recorded on an IBM FT-IR spectrometer. Spectra were taken of neat films on NaCl plates. UV/vis spectra were recorded on a Perkin-Elmer Lambda 6 instrument. Spectral grade THF was used as a solvent for the polymers, whereas spectral grade *n*-hexane was used as a solvent for the monomers. When appropriate, thin films of polymer were prepared on a flat quartz surface from dilute chloroform solutions.

The molecular weight distribution of the polymers was determined by GPC on a Waters system. This was comprised of a U6K injector, a 510 HPLC solvent delivery system, an R401 differential refractometer, and a Maxima 820 control system. A Waters 7.8 mm × 30 cm Ultrastyragel linear column packed with <10-μm particles of mixed pore size cross-linked styrene–divinylbenzene copolymer maintained at 20 °C was used for analysis. The eluting solvent was HPLC grade THF at a flow rate of 0.7 mL/min. Retention times were calibrated both before and after sample runs against known monodisperse polystyrene standards.

Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGS-2 instrument. The temperature was calibrated with ferromagnetic standards and the weight was calibrated on the 100-mg scale. The temperature program for the analysis was 50 °C for 10 min followed by an increase of 5 °C/min to 800 °C. These runs were conducted in nitrogen at a flow rate of 40 cm^3/min.

The thermal transitions of the polymers were determined by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC-7 fitted with a complete glovebox. The instrument was calibrated at high temperature with indium (mp 156 °C) and at low temperature with spectral quality *n*-hexane (mp −95 °C) or deionized water (mp 0 °C). Cooling and heating cycles were all done at 10 °C/min under nitrogen unless otherwise noted. The samples were annealed at 10 °C for 30 min followed by a cooling cycle to −65 °C. The samples were allowed to equilibrate at −65 °C for 10 min and then were heated to 160 °C. Cooling runs were conducted after the second heating run.

Polarizing optical microscopy (POM) was done using a Unitron polarizing microscope fitted with a Leitz/Omega hot stage for above room temperature work and a custom fabricated cold stage for the range −20 to −25 °C. Fiber samples were melted on a slide at 80 °C and annealed at 25 °C for 24 h. The opaque films were heated to 80 °C and then cooled at 0.5 °C/min. Micrographs

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Scheme I. Preparation of Poly[1-methyl-1-(3′-phenoxypropyl)-1-sila-*cis*-pent-3-ene] (VI)

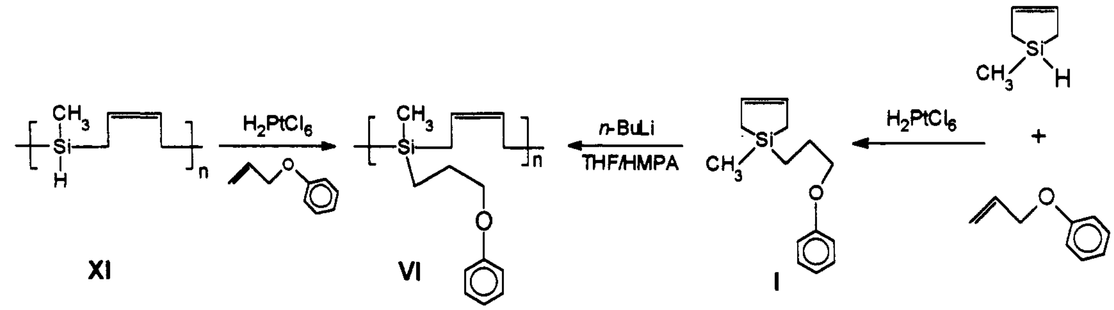
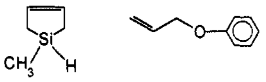
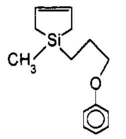
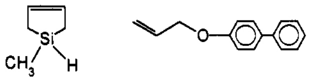
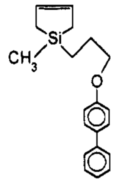
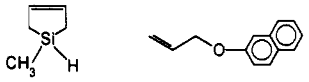
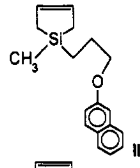
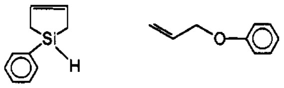
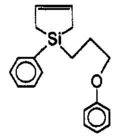
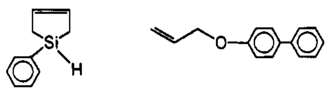
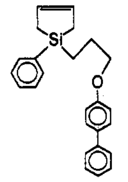


Table I. Monomers Synthesized

Starting Materials	Monomers	Yields
	 I	84%
	 II	70%
	 III	72%
	 IV	88%
	 V	80%

were obtained at various temperatures at a magnification of 100× with a Polaroid camera attachment.

Wide-angle X-ray diffraction (WAXD) patterns of pulverized samples of fiber were obtained on a Rigaku RE-2000 instrument. The X-ray patterns (Ni-filtered Cu radiation) were measured for powder samples at 25 °C.

Scanning electron micrographs (SEM) of the polymer samples were obtained on a Cambridge Stereoscope-360 instrument at 10 keV. Samples were mounted with graphite and sputtered coated with gold. Micrographs were obtained at various magnifications (70–30000×) at room temperature. The coated polymer samples were stable to the beam throughout the measurement range.

Low-resolution mass spectra were obtained on a Finnigan MAT Incos 50 GCMS instrument at an ionizing voltage of 70 eV. A 0.25 mm × 30 m fused-silica DB-5 capillary column was used in the gas chromatographic inlet of the mass spectrometer. High-resolution mass spectra were obtained at the University of California Riverside Mass Spectrometry Facility on a VG-7070 EHF mass spectrometer at an ionizing voltage of 20 eV. Exact masses were determined by peak matching against known masses of perfluorokerosene.

Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN, or Oneida Research Services, Whitesboro, NY.

THF was freshly distilled from a dark blue solution of sodium benzophenone ketyl under nitrogen. HMPA was distilled over calcium hydride and stored over sieves (4 Å) in a septum-sealed container. Chloroplatinic acid was purchased from Aldrich and was used without further purification. *n*-Butyllithium was purchased from Aldrich and was titrated before use.[11] Allyl phenyl ether was purchased from Aldrich and was redistilled before use. 4-(Allyloxy)biphenyl,[12] 2-(allyloxy)naphthalene,[13] 1-methyl-1-silacyclopent-3-ene,[14] 1-phenyl-1-silacyclopent-3-ene,[15] and 1,1-diphenyl-1-silacyclopent-2-ene[16] were prepared by literature procedures.

All reactions were conducted in flame-dried glassware under an atmosphere of ultrahigh-purity argon.

Monomer Synthesis. Monomers were prepared by hydrosilation reactions of 1-methyl-1-silacyclopent-3-ene[14] or 1-phenyl-1-silacyclopent-3-ene[15] and the corresponding allyl aryl ethers. A typical procedure is given below.

1-Methyl-1-(3′-(*p*-biphenylyloxy)propyl)-1-silacyclopent-3-ene (II). A 15-mL round-bottom flask containing a Teflon-covered magnetic stirring bar was charged with 1.0 g (4.8 mmol) of 4-(allyloxy)biphenyl and 0.56 g (5.7 mmol) of 1-methyl-1-silacyclopent-3-ene. The flask was fitted with a rubber septum. Chloroplatinic acid (2.0 mg) dissolved in 1 mL of THF was added by syringe. This amounts to approximately 1 × 10^{-3} platinum to allyl aryl ether. An exothermic reaction ensued such that within 10 min the mixture was transformed into a dark orange–black oil. The reaction was allowed to stir at room temperature for a total of 2 h. The flask was fitted with a reflux condenser and heated at 65 °C for an additional 2 h. The reaction was quenched via the addition of a water/methanol solution and was allowed to stand in order to separate the aqueous and organic phases.

The organic layer was removed and the aqueous phase was extracted with ether (2 × 50 mL). The combined organic phases were dried over anhydrous $CaCl_2$, filtered through a plug of glass wool, and then concentrated under reduced pressure to yield a dark brown viscous oil. The monomer mixture was purified and removed from the Pt complexes by flash chromatography on a silica gel column using pentane/chloroform (1:1) as eluant. This was repeated twice. In this manner, a water-white liquid was obtained in 70% yield. Table I illustrates the monomers which were prepared.

In the case of 1-methyl-1-(3′-phenoxypropyl)-1-silacyclopent-3-ene (I) a mixture of 2-ene (5%) and 3-ene (95%) was obtained (Figure 1). In no other case was the 2-ene isomer detected.

Characterization of Monomers. 1-Methyl-1-(3′-phenoxypropyl)-1-silacyclopent-3-ene (I). ^1H NMR δ 0.07 (s, 3 H), 0.66 (m, 2 H), 1.18 (m, 4 H), 1.69 (m, 2 H), 3.77 (t, 2 H, J = 6.7 Hz), 5.74 (s, 2 H), 6.77 (m, 3 H), 7.13 (m, 2 H). ^{13}C NMR δ −3.72, 10.78, 16.39, 23.98, 70.09, 114.36, 120.40, 129.32, 130.92, 158.96. ^{29}Si NMR δ 18.74. UV/vis λ_{max} (ϵ) 220.9 (11 600), 266.8 (1850), 271.3 (2520), 277.9 (2190) nm. IR ν 3063, 3018, 2912, 1601, 1586, 1470, 1456, 1436, 1402, 1387, 1336, 1302, 1289, 1245, 1204, 1172, 1154, 1100, 1080, 1035, 1015, 993, 944, 891, 843, 753, 725 cm^{-1}. GC/MS *m/e* (relative intensity) 232 (19) $M^{\cdot+}$, 190 (7), 175 (46), 150 (100), 135 (61), 121 (55), 97 (27), 77 (40), 55 (12). High-resolution MS *m/e* calcd for $C_{14}H_{20}OSi$: 232.1283. Found: 232.1271. Elemental Anal. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67. Found: C, 73.15; H, 8.80.

1-Methyl-1-(3′-phenoxypropyl)-1-silacyclopent-2-ene. ^1H NMR δ −0.01 (m, 3 H), 0.58 (m, 2 H), 1.08 (m, 4 H), 1.53 (m, 2 H), 3.75 (m, 2 H), 5.15 (m, 1 H), 5.73 (m, 1 H), 6.72 (m, 3 H), 7.09 (m, 2 H). ^{13}C NMR δ 7.13, 11.74, 16.42, 24.10, 32.08, 70.22, 114.44, 120.44, 128.88, 129.34, 153.88, 159.61. ^{29}Si NMR δ 20.41. GC/

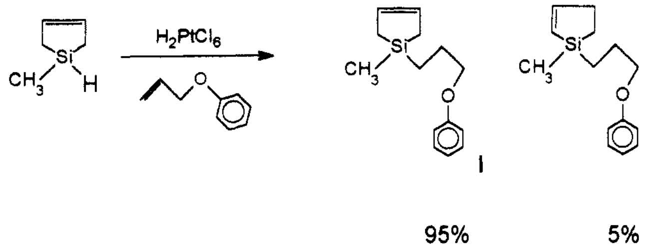


Figure 1. Preparation of 1-methyl-1-(3′-phenoxypropyl)-1-silacyclopent-3-ene (I).

MS *m/e* (relative intensity) 232 (22) $M^{\cdot+}$, 190 (36), 175 (100), 162 (10), 149 (8), 121 (30), 97 (78), 77 (21), 69 (15), 55 (10).

1-Methyl-1-(3′-(*p*-biphenylyloxy)propyl)-1-silacyclopent-3-ene (II). ^{1}H NMR δ 0.06 (s, 3 H), 0.65 (m, 2 H), 1.18 (m, 4 H), 1.70 (m, 2 H), 3.77 (t, 2 H, J = 6.6 Hz), 5.75 (s, 2 H), 6.82 (m, 2 H), 7.10–7.42 (br m, 7 H). ^{13}C NMR δ −3.70, 10.77, 16.41, 23.98, 70.24, 114.67, 126.50, 126.57, 127.99, 128.62, 130.98, 133.42, 140.74, 158.56. ^{29}Si δ 18.82. UV/vis λ_{max} (ϵ) 210.6 (29 900), 260.0 (24 600) nm. IR ν 3061, 3017, 2923, 2882, 1888, 1671, 1609, 1585, 1570, 1519, 1488, 1472, 1451, 1400, 1290, 1270, 1242, 1204, 1185, 1175, 1100, 1043, 1030, 1013, 1004, 994, 944, 892, 833, 786, 763, 721 cm^{-1}. GC/MS *m/e* (relative intensity) 308 (65) $M^{\cdot+}$, 266 (35), 254 (47), 239 (32), 226 (100), 197 (68), 181 (4), 152 (43), 127 (4), 97 (41), 69 (12), 55 (9). High-resolution MS *m/e* calcd for $C_{20}H_{24}OSi$: 308.1596. Found: 308.1586.

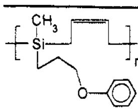
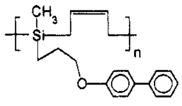
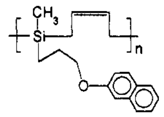
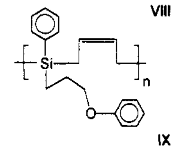
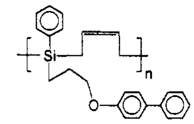
1-Methyl-1-(3′-β-naphthoxypropyl)-1-silacyclopent-3-ene (III). ^{1}H NMR δ 0.08 (s, 3 H), 0.69 (m, 2 H), 1.20 (m, 4 H), 1.73 (m, 2 H), 3.87 (t, 2 H, J = 6.6 Hz), 5.76 (s, 2 H), 6.98–7.30 (br m, 4 H), 7.60 (m, 2 H). ^{13}C NMR δ −3.65, 10.87, 16.44, 23.96, 70.21, 106.47, 118.93, 123.42, 126.24, 126.65, 127.59, 128.85, 129.28, 132.04, 156.96. ^{29}Si NMR δ 18.69. UV/vis λ_{max} (ϵ) 262.0 (7360), 272.0 (7820), 283.4 (5650), 315.8 (2370), 328.4 (2910) nm. IR ν 3058, 3016, 2880, 1780, 1737, 1726, 1703, 1698, 1687, 1677, 1673, 1650, 1630, 1601, 1574, 1552, 1524, 1512, 1464, 1441, 1435, 1390, 1357, 1268, 1258, 1217, 1182, 1120, 1100, 1016, 944, 866, 840, 810, 784, 746, 723 cm^{-1}. GC/MS *m/e* (relative intensity) 282 (63) $M^{\cdot+}$, 241 (20), 228 (25), 213 (45), 200 (100), 185 (37), 171 (52), 141 (26), 127 (59), 115 (45), 97 (41), 85 (8), 71 (16), 55 (13). High-resolution MS *m/e* calcd for $C_{18}H_{22}OSi$: 282.1440. Found: 282.1443.

1-Phenyl-1-(3′-phenoxypropyl)-1-silacyclopent-3-ene (IV). ^{1}H NMR δ 0.97 (m, 2 H), 1.46 (m, 4 H), 1.76 (m, 2 H), 3.79 (t, 2 H, J = 6.6 Hz), 5.83 (m, 2 H), 6.78 (m, 3 H), 7.20 (m, 5 H), 7.43 (m, 2 H). ^{13}C NMR δ 9.26, 15.83, 23.95, 69.98, 114.43, 120.46, 127.88, 129.27, 129.35, 131.06, 133.87, 136.83, 158.95. ^{29}Si NMR δ 13.72. UV/vis λ_{max} (ϵ) 219.8 (16 870), 265.4 (1840), 271.2 (2330), 278.0 (1950) nm. IR ν 3068, 3018, 2918, 2883, 2780, 1601, 1587, 1498, 1471, 1429, 1402, 1336, 1302, 1290, 1245, 1203, 1172, 1154, 1114, 1100, 1079, 1035, 1016, 993, 944, 887, 808, 789, 755 cm^{-1}. GC/MS *m/e* (relative intensity) 294 (24) $M^{\cdot+}$, 253 (3), 240 (5), 223 (4), 212 (100), 197 (43), 174 (12), 159 (19), 134 (26), 121 (24), 105 (41), 77 (24), 65 (8), 53 (11). High-resolution MS *m/e* calcd for $C_{19}H_{22}OSi$: 294.1440. Found: 294.1446.

1-Phenyl-1-(3′-(*p*-biphenylyloxy)propyl)-1-silacyclopent-3-ene (V). ^{1}H NMR δ 0.95 (m, 2 H), 1.41 (m, 4 H), 1.68 (m, 2 H), 3.79 (t, 2 H, J = 6.6 Hz), 5.78 (s, 2 H), 6.79 (m, 2 H), 6.82–7.31 (br m, 12 H). ^{13}C NMR δ 9.26, 15.83, 23.95, 70.21, 114.68, 126.56, 126.65, 127.87, 127.91, 128.06, 128.66, 129.30, 131.08, 133.89, 136.92, 140.96, 159.02. ^{29}Si NMR δ 13.65. UV/vis λ_{max} (ϵ) 218.5 (28 700), 263.3 (25 100) nm. IR ν 3070, 3022, 3010, 2948, 2835, 1608, 1521, 1489, 1472, 1452, 1401, 1287, 1271, 1251, 1202, 1176, 1157, 1113, 1102, 1022, 1010, 994, 946, 911, 837, 810, 789 cm^{-1}. GC/MS *m/e* (relative intensity) 370 (71) $M^{\cdot+}$, 328 (26), 316 (41), 288 (100), 273 (39), 228 (9), 197 (39), 159 (53), 141 (18), 105 (77), 93 (11), 81 (15), 53 (8). High-resolution MS *m/e* calcd for $C_{25}H_{26}OSi$: 371.1753. Found: 371.1753.

Polymer Synthesis by Anionic Ring-Opening Polymerization. High Molecular Weight Poly[1-methyl-1-(3′-phenoxypropyl)-1-sila-*cis*-pent-3-ene] (VI). A 25-mL round-bottom flask containing a Teflon-covered magnetic stirring bar was fitted with a rubber septum. THF (10 mL), 100 μL of HMPA, and 0.50 g of I were added by syringe. The flask was immersed in a dry ice/acetone bath and the mixture was allowed to stir at low temperature for 15 min. *n*-Butyllithium (120 μL) was added via syringe, and the mixture turned a dark red color. The reaction was allowed to proceed for 3 h, at which time it was quenched via the addition of saturated aqueous NH_4Cl. The organic phase was removed, and the aqueous phase was extracted with ether (3 × 50 mL). The combined organic phases were washed with water, dried over anhydrous $CaCl_2$, and filtered through a plug of glass wool. The solvents were removed under reduced pressure, yielding an opaque, gummy solid. The polymer was twice taken up in a minimum amount of THF, precipitated out of solution with methanol, and then centrifuged. Finally, the polymer was dried on a high-vacuum line, giving 0.43 g of material (86% yield). The supernatant from the polymer precipitation was combined and concentrated under vacuum to give highly enriched 2-isomer. All anionic ring-opening polymerizations leading to high molecular weight VII, VIII, IX, and X were carried out as above except that no 2-ene isomer was detected in either the starting monomer or the supernatant liquid after the precipitation of VII, VIII, IX, and X. Table II illustrates the polymers which were prepared.

Table II. Polymers Synthesized

Polymer	Yield	M_w/M_n	Thermal Transitions(°C)		
			T_g	T_m	T_i
 VI	80%	241900/149600	-31	–	–
 VII	95%	52700/29000	10	42	61
 VIII	93%	17200/8460	-1	–	–
 IX	88%	29100/16700	-5	10 to 23	
 X	87%	13600/7130	–	12	21

Characterization of Polymers. High Molecular Weight Poly[1-methyl-1-(3′-phenoxypropyl)-1-sila-*cis*-pent-3-ene] (VI). GPC M_w/M_n = 241900/149600. ^{1}H NMR δ −0.18 (s, 3 H), 0.45 (m, 2 H), 1.28 (m, 4 H), 1.60 (m, 2 H), 3.67 (t, 2 H, J = 6.8 Hz), 5.13 (m, 2 H), 6.70 (m, 3 H), 7.06 (m, 2 H). ^{13}C NMR δ −5.29, 9.58, 14.92, 23.80, 70.45, 114.43, 120.43, 123.08, 129.38, 159.00. ^{29}Si NMR δ 3.42. UV/vis λ_{max} (ϵ) 266.4 (2220), 271.8 (2710), 278.2 (2010) nm. IR ν 3007, 2929, 2876, 1601, 1586, 1498, 1471, 1412, 1377, 1302, 1289, 1246, 1172, 1153, 1079, 1035, 993, 929, 890, 846, 752, 691 cm^{-1}. Elemental Anal. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67. Found: C, 70.73; H, 7.68. DSC T_g = −31 °C, no T_m. TGA Onset 412 °C, 50% decomposition 440 °C; 19% char yield at 800 °C.

Poly[1-methyl-1-(3′-(*p*-biphenylyloxy)propyl)-1-sila-*cis*-pent-3-ene] (VII). GPC M_w/M_n = 52700/29000. ^{1}H NMR δ −0.16 (s, 3 H), 0.47 (m, 2 H), 1.31 (m, 4 H), 1.63 (m, 2 H), 3.69 (t, 2 H, J = 6.6 Hz), 5.15 (m, 2 H), 6.72 (m, 2 H), 7.06–7.33 (br m, 7 H). ^{13}C NMR δ −5.24, 9.65, 14.96, 23.86, 70.66, 114.73, 123.12, 126.56, 126.63, 128.05, 128.70, 133.41, 140.77, 154.62. ^{29}Si NMR δ 3.45. UV/vis λ_{max} (ϵ) 221.1 (38 100), 263.8 (30 900) nm. IR ν 3060, 3032, 2932, 2876, 1675, 1638, 1609, 1584, 1569, 1519, 1488, 1472, 1451, 1411, 1377, 1311, 1290, 1270, 1246, 1186, 1176, 1151, 1113, 1100, 1044, 1025, 1013, 1004, 994, 909, 892, 834, 762, 733 cm^{-1}. Elemental Anal. Calcd for $C_{20}H_{24}OSi$: C, 77.87; H, 7.84.

Found: C, 75.58; H, 7.92. DSC T_g = 10 °C, T_m = 42 °C, T_i = 61 °C. TGA Onset 417 °C, 50% decomposition 455 °C, 20% char at 800 °C.

Poly[1-methyl-1-(3′-*β*-napthoxypropyl)-1-sila-*cis*-pent-3-ene] (VIII). GPC M_w/M_n = 17200/8460. ^{1}H NMR δ −0.15 (s, 3 H), 0.50 (m, 2 H), 1.34 (m, 4 H), 1.67 (m, 2 H), 3.60 (m, 2 H), 5.17 (s, 2 H), 7.10 (m, 4 H), 7.51 (m, 3 H). ^{13}C NMR δ −5.29, 9.62, 14.92, 23.74, 70.51, 106.46, 118.90, 123.08, 123.39, 126.22, 126.62, 127.58, 128.80, 129.26, 134.55, 156.94. ^{29}Si NMR δ 3.50. UV/vis λ_{max} (ϵ) 262.2 (9720), 272.4 (10 300), 284.1 (7750), 314.8 (3230), 329.0 (4040). IR ν 3058, 3007, 2932, 2877, 1632, 1602, 1580, 1512, 1466, 1441, 1389, 1356, 1260, 1219, 1181, 1120, 1019, 964, 921, 910, 844, 747 cm^{-1}. Elemental Anal. Calcd for $C_{18}H_{22}OSi$: C, 76.54; H, 7.85. Found: C, 74.93; H, 7.97. DSC T_g = −1 °C, no T_m. TGA Onset 430 °C, 50% decomposition 465 °C, 5% char yield at 800 °C.

Poly[1-phenyl-1-(3′-phenoxypropyl)-1-sila-*cis*-pent-3-ene] (IX). GPC M_w/M_n = 29100/16700. ^{1}H NMR δ 0.88 (m, 2 H), 1.63–1.83 (br m, 6 H), 3.80 (t, 2 H, J = 6.6 Hz), 5.31 (m, 2 H), 6.84 (m, 3 H), 7.23 (m, 3 H), 7.17–7.45 (br m, 7 H). ^{13} NMR δ 8.09, 13.65, 23.67, 70.23, 114.43, 120.41, 123.32, 127.72, 129.12, 129.34, 134.09, 136.30, 158.95. ^{29}Si NMR δ −3.87. UV/vis λ_{max} (ϵ) 265.4 (1600), 271.0 (1540), 278.4 (1140) nm. IR ν 3069, 3042, 3009, 2930, 2876, 1637, 1601, 1586, 1497, 1470, 1427, 1417, 1377, 1335, 1302, 1290, 1244, 1172, 1111, 1079, 1033, 910, 885, 824, 754, 735 cm^{-1}. Elemental Anal. Calcd $C_{19}H_{22}OSi$: C, 77.50; H, 7.53. Found: C, 77.51; H, 8.10. DSC T_g = −5 °C, multiple transitions between 10 and 23 °C. TGA Onset 415 °C, 50% decomposition 475 °C, 25% char at 800 °C.

Poly[1-phenyl-1-(3′-(*p*-biphenylyloxy)propyl)-1-sila-*cis*-pent-3-ene] (X). GPC M_w/M_n = 13600/7130. ^{1}H NMR δ 0.96 (br m, 2 H), 1.73 (br m, 6 H), 3.86 (br m, 2 H), 5.39 (s, 2 H), 6.91 (br m, 2 H), 7.33–7.52 (br m, 12 H). ^{13}C NMR δ 8.08, 13.62, 23.67, 70.37, 114.66, 123.32, 126.52, 126.59, 127.73, 127.99, 128.64, 129.15, 133.36, 134.07, 136.23, 140.71, 158.50. ^{29}Si NMR δ −3.93. UV/vis λ_{max} (ϵ) 226.2 (30 000), 258.7 (29 600). IR ν 3068, 3030, 3009, 2926, 2875, 1609, 1584, 1568, 1551, 1518, 1486, 1470, 1451, 1428, 1411, 1377, 1290, 1245, 1185, 1174, 1112, 1044, 1028, 1013, 1004, 909, 888, 833 cm^{-1}. Elemental Anal. Calcd for $C_{25}H_{26}OSi$: C, 81.04; H, 7.08. Found: C, 80.41; H, 6.97. DSC No T_g, T_m = 12 °C, T_i = 21 °C. TGA Onset 421 °C, 50% decomposition 470 °C, 17% char yield at 800 °C.

Polymer Synthesis by Graft Hydrosilation Chemistry. Poly(1-methyl-1-sila-*cis*-pent-3-ene) (XI) was prepared by anionic ring-opening polymerization of 1-methyl-1-silacyclopent-3-ene. It had spectral properties identical to those reported[14] and M_w/M_n = 1390/980.

Low Molecular Weight Poly[1-methyl-1-(3′-phenoxypropyl)-1-sila-*cis*-pent-3-ene] (VI). To a 50-mL conical flask, used to prevent foaming, containing a Teflon-covered magnetic stirring bar were added 0.50 g (5.1 mequiv) of XI and allyl phenyl ether (1.0 g, 7.5 mmol). The flask was fitted with a rubber septum, and the mixture was stirred at room temperature for 5 min. Chloroplatinic acid (1 mg dissolved in 1 mL of THF) was added by syringe. The reaction mixture was stirred at room temperature for 24 h. The reaction mixture did not turn dark black. After 24 h, the reaction was quenched with methanol, and the solvents were removed on a high-vacuum line. The remaining thick viscous liquid was dissolved in 1 mL of THF and precipitated with 4 mL of methanol. The polymer was centrifuged and then dried on a high-vacuum line. ^{1}H and ^{13}C NMR showed that all available Si–H groups had reacted and that no unreacted allyl phenyl ether remained. Due to the low molecular weight of the material, polymer end groups were observed in the NMR. GPC M_w/M_n = 2380/1560. ^{1}H NMR δ −0.15 to −0.07 (br m, 3 H), 0.53 (m, 2 H), 1.15–1.31 (br m, 4 H), 1.67 (m, 2 H), 3.73 (m, 2 H), 5.13 (s, 2 H), 6.74 (m, 3 H), 7.10 (m, 2 H). ^{13}C NMR δ −5.45, −5.01, 0.97, 9.40, 9.60, 13.77, 14.92, 19.67, 23.76, 26.63, 70.39, 114.44, 120.42, 122.64, 122.71, 122.80, 129.35, 158.99. Elemental Anal. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67. Found: C, 71.83; H, 8.23. DSC T_g = −29 °C, no T_m. TGA Onset 380 °C, 50% decomposition 440 °C, 20% char at 800 °C.

Attempted Polymerization of 1,1-Diphenyl-1-silacyclopent-2-ene (XII). Treatment of a pure sample of XII under the anionic ring-opening polymerization conditions employed above produced no reaction, and starting material was recovered.

Results and Discussion

Anionic ring-opening polymerization of 1-silacyclopent-3-enes has been utilized in the preparation of materials with a range of physical properties.[8,17-19] Changes in pendant groups of the monomer invariably lead to variation of the bulk properties of the polymer. To better understand the relationship between the side chain and the morphology of such polymeric materials, we have prepared a number of novel monomers and polymers with different, but structurally analogous, 3′-(aryloxy)propyl side chains.

In the synthesis of I, a mixture of 2-ene and 3-ene (I) isomers was obtained (Figure 1). The 2-ene isomer may result from Pt-catalyzed isomerization of the 3-ene (I) to 2-ene isomers. The high temperature required for distillation in the presence of Pt favors the isomerization process. For this reason, it is recommended that monomers of this type not be purified by distillation. Purification can be achieved with little or no isomerization by flash chromatography. The presence of the 2-ene isomer apparently does not hinder, in any detectable way, the anionic ring-opening polymerization of the 3-ene isomer. High molecular weight material, with the expected cis stereochemistry, was obtained. The lack of reactivity of 2-ene isomer was confirmed by an independent experiment on XII. It is known that 1,1-diphenyl-1-silacyclopent-3-ene can be polymerized readily under anionic conditions.[17] Similar experiments on XII yielded no reaction, and the starting material was recovered. These facts are consistent with the mechanism proposed for the polymerization reaction.

Thus polymerization of silacyclopent-3-enes, as illustrated in Figure 2, involves attack by an alkyllithium reagent on silicon, resulting in a hypervalent pentacoordinate siliconate species.[19] The ring opening yiels an allylic anion which reacts with the silyl center of another molecule of monomer to yield a new hypervalent siliconate species. This series of reactions constitute the propagation pathway leading to high polymer. Polymerization of a silacyclopent-2-ene would entail ring opening to produce a less stable vinylic or primary carbanion. This apparently is not thermodynamically favored. While the failure of silacyclopent-2-enes to undergo polymerization is not unexpected, the fact that no reaction is observed is surprising since the addition of alkyllithiums to vinylsilanes is well known.[18,20]

A linear relationship between the length of the pendant groups in poly(1-methyl-1-silacyclopent-3-enes) and the T_g is observed. These data are plotted in Figure 3. Such relationships are know for other polymer systems.[21] Polymers VI, VIII, IX, and X are tacky clear liquids at room temperature (~25 °C). Fibers can be drawn from polymers VII–X at room temperature. Polymer VII is a glassy bluish-white solid at room temperature. Strong stable white fibers of up to several meters in length can be drawn from the melt of VII. The DSC of VII is given in Figure 4. The fibers of VII after melting and annealing for 2 months at room temperature show a T_g at 10 °C, an exotherm at 25 °C due to cold crystallization,[23] a T_m at 42 °C, and a T_i at 61 °C. On cooling, two exothermic transitions are observed. The concentration of thermal events within an ~30 °C range from T_g to T_m makes the DSC of VII quite remarkable.

In Figure 5, POM micrographs of VII are shown. Liquid crystalline textures were observed for this polymer between 40 and 60 °C (Figure 5A). The formation of this mesophase is consistent with the results obtained by DSC. The oriented fiber of VII was melted and annealed at 80 °C and slowly cooled to room temperature. The mesophase

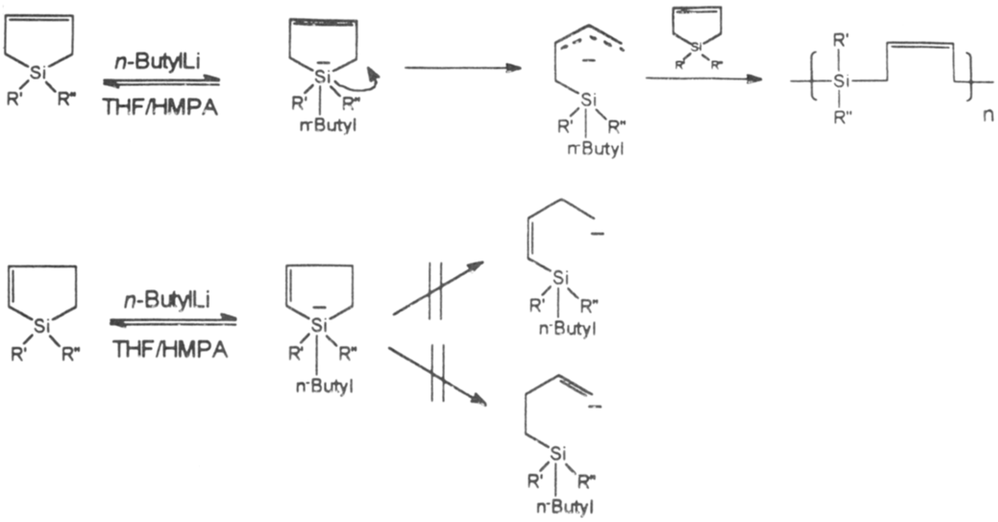


Figure 2. Mechanism of anionic ring-opening polymerization of 1-silacyclopent-3-enes and reaction of 1-silacyclopent-2-enes with *n*-butyllithium.

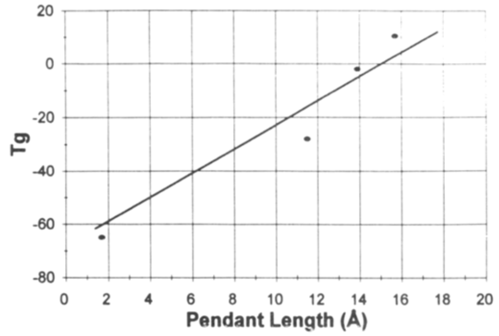


Figure 3. Linear relationship between the 3′-(aryloxy)propyl side chain length and the T_g for poly(1-methyl-sila-*cis*-pent-3-enes).

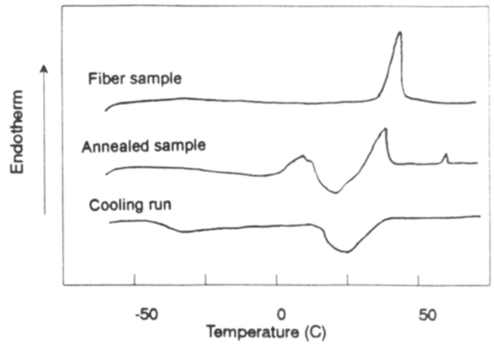


Figure 4. DSC of VII.

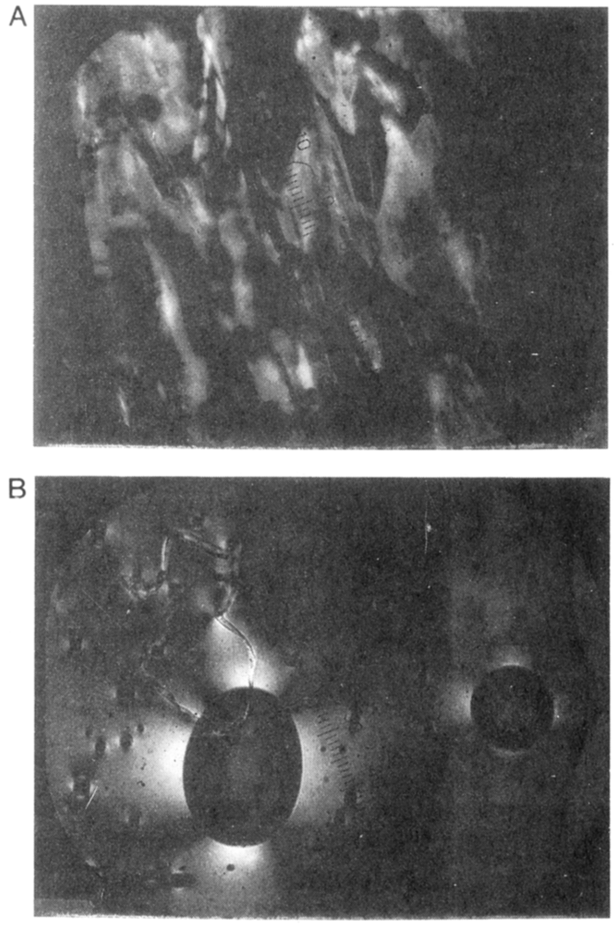


Figure 5. POM textures of VII viewed under cross polarizers (all photos at 100×): (A) 45 °C; 25 °C after coverslip displacement.

formed from the isotropic phase has a colored schlieren texture under cross polarizers. The smectic phase was stable from 61 to 42 °C. At 25 °C, when the slide cover was displaced the polymer turned an opaque-bluish color. The opaque sample gave a birefringent texture under cross polarizers at 25 °C (Figure 5B), indicative of crystallization. The sample very slowly forms an opaque-blue solid on the microscope slide without the external force being applied. In either case, the sample had the same textures under cross polarizers.

When VII was cooled below room temperature, the bulk sample turned a darker sky blue color. This color was a result of reflected light only; light transmitted through the sample had a distinct yellow color. Extremely tough thin films of the polymer, prepared for UV/vis analysis, show multiple shoulders near 400 nm when compared to the solution spectra as shown in Figure 6. These shoulders are thought to be due to selective scattering of near-visible light and are probably not due to any inherent chromophore. If the sample is cooled at −10 °C for 30 min, it starts to become birefringent to normal incandescent light. These optical features, birefringence and blue phase, of the polymer sample are fragile. Heating the sample slightly above −10 °C causes the birefringence to disappear, and heating the sample above 25 °C causes the blue phase to disappear.

The appearance of a blue-colored phase below the isotropic temperature in liquid crystalline polymers has previously been observed for cholesteric materials.[2] In

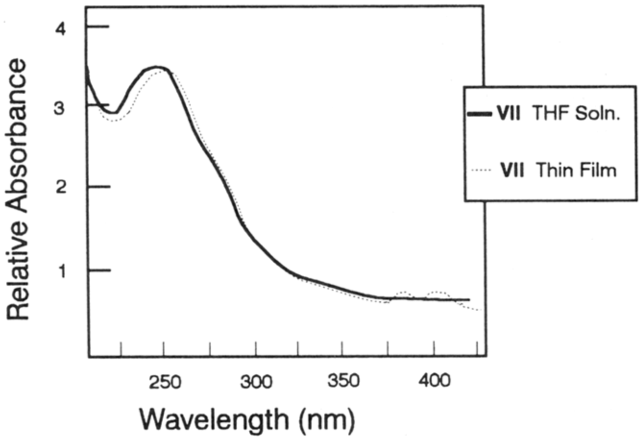


Figure 6. UV/vis data for VII in THF solution and as a thin-film solid.

fact, the appearance of this phenomenon is characteristic of a cholesteric phase. The only possible site of chirality in our material is the silyl centers and not the mesogenic group. Cholesteric side chain liquid crystals usually have chirality associated with the pendant mesogenic groups. While it is possible that the blue coloration is associated with the twisting of the isotactic carbosilane backbone, we have no definitive evidence of this. Therefore, we believe that the optical behavior of VII is not associated with the formation of a cholesteric phase.

The presence of small crystallites in the opaque-blue polymer solid VII, confirmed by SEM (Figure 7), may account for the blue color observed. It is important to note that the oriented fiber of VII does not show a blue phase or birefringence at any temperature. In addition, the fiber sample does not show the presence of any microcrystallites. No overall order at the surface in the fiber sample is seen at the level resolvable with SEM. We believe that the blue relfected light results from the crystallites acting like a diffraction source within the sample. These spherulite particles (Figure 7B) are remarkably uniform within the sample, having an average particle size of 70 nm. Such observations have been made for other polymer systems.[24] As the sample is cooled the crystallites may be formed in higher density throughout the polymer sample. Hence, the sample turns darker blue. Birefringence may result if the spherulites coalesce at lower temperature to form particles whose size is on the order of the wavelength of light.

The DSC data for VI and VIII show only T_gs. These polymers form fibers at room temperature which relax over a few hours back to the viscous liquid state. Annealing VI for 24 h at −5 °C and VIII for 24 h at 20 °C showed no melting endotherms. These polymers exhibited no liquid crystalline behavior.

Stable fibers can also be drawn from the melt of polymer IX. The DSC (Figure 8) of these fibers shows the presence of multiple transitions above T_g. Samples annealed at temperatures above these transitions show only a single T_g. A cooling cycle showed at least two exotherms. The nature of the multiple endotherms in the DSC of the fiber is not known. POM of IX did not confirm the existence of liquid crystalline phases above T_g. Further studies into these low-temperature phase transitions are underway.

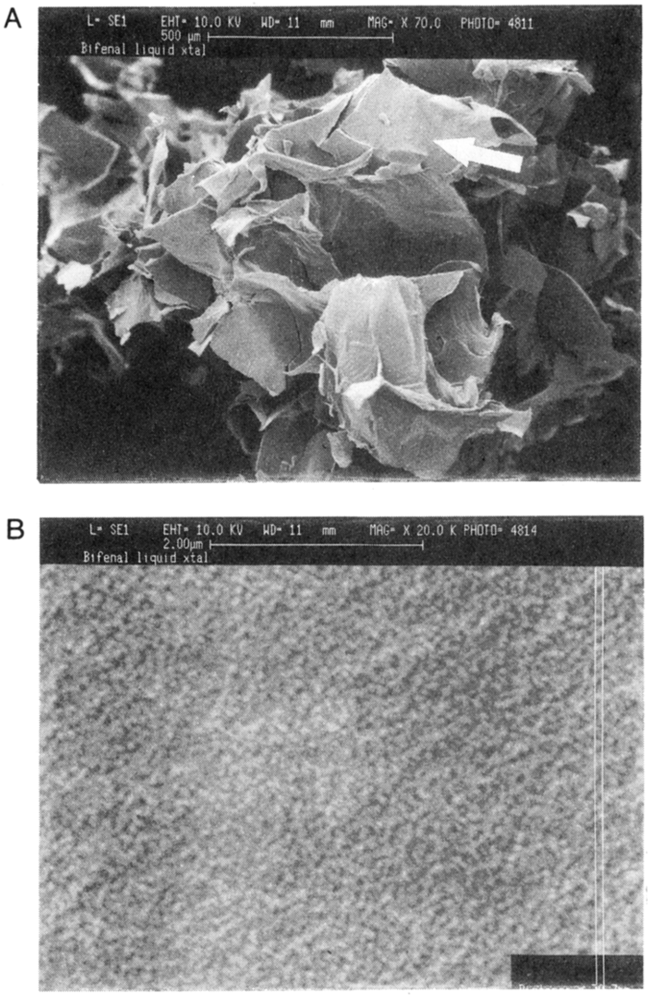


Figure 7. SEM of a glassy blue-white VII sample at 25 °C. (A) SEM of glassy sample (70×). The arrow indicates the area of further magnification. (B) SEM of the microcrystallites (20000×). The distance between the lines at the right of the photo is ~70 nm.

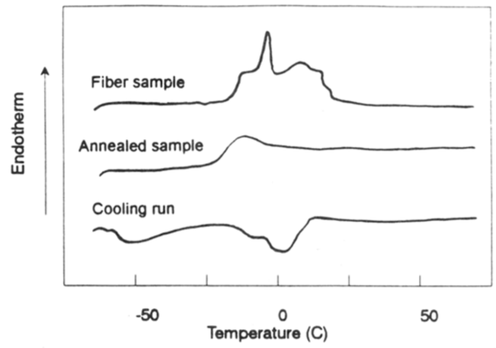


Figure 8. DSC of IX.

The DSC of X is given in Figure 9. Heating the pulverized fiber sample shows two closely spaced endotherms at 12 and 21 °C. The first endotherm is assigned as T_m and the second as T_i.[2–5,8] Further heating runs on the annealed sample show a broad endotherm between 10 and 30 °C. Annealing the sample at −10 °C for 24 h again shows both a T_m and a T_i. A cooling cycle shows two exotherms. Such details are common features of liquid crystalline (LC) materials.[2,3] POM of the sample cooled between T_m and T_i revealed no information about the nature of the LC phase. WAXD of X at 25 °C shows two broad peaks as illustrated in Figure 10. The diffuse small-angle spacing may be due to some residual LC-like ordering.[5] However, no sharp peaks due to crystalline reflections are observed. Therefore, the fiber formed of this sample is metastable with a long relaxation time.

In contrast, WAXD of VII at room temperature shows the sample to be highly crystalline. Integration of sharp peaks to baseline noise[25] indicates that VII is approximately 70% crystalline. As illustrated in Figure 11A, a

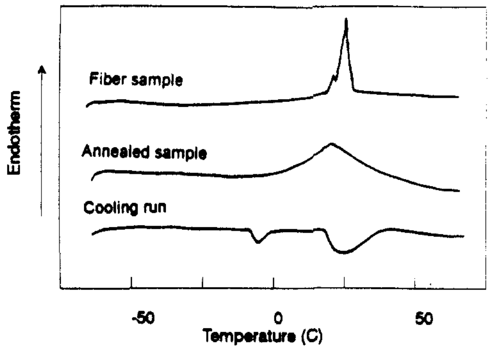


Figure 9. DSC of X.

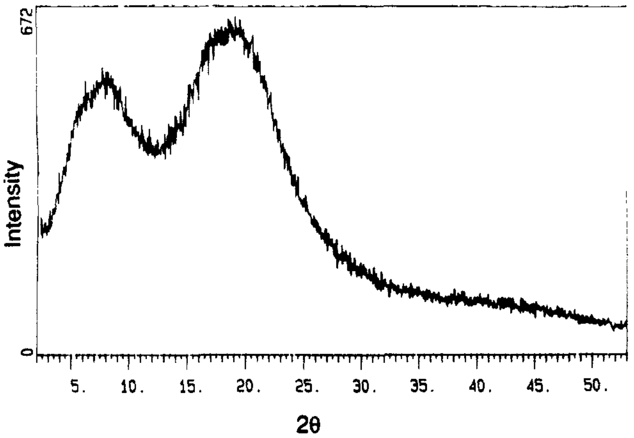


Figure 10. WAXD of X at 25 °C.

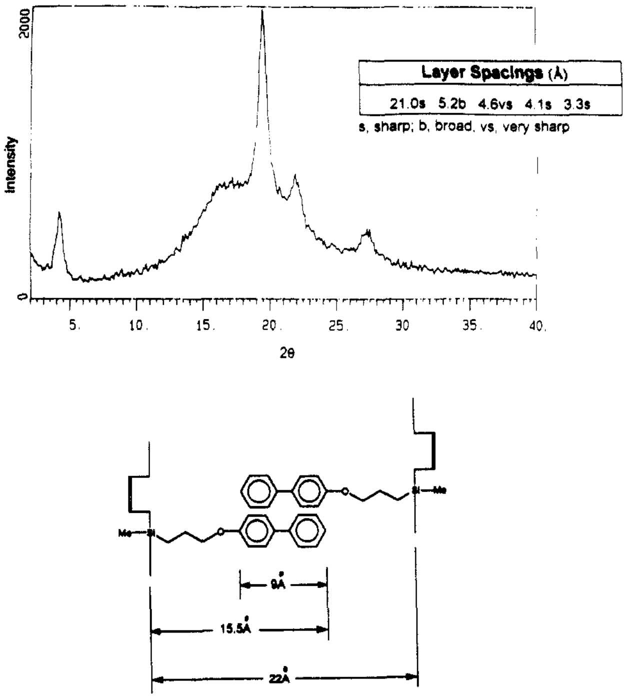


Figure 11. WAXD and possible crystal reflections for VII. (A) WAXD data for VII at 25 °C. (B) *d*-Spacing data indicate that VII has significant interdigitation or tilting.

sharp low-angle spacing corresponding to 21.0 Å is seen. In addition, many sharp high-angle lines between 3.3 and 4.6 Å are present along with a broad peak centered near 5.2 Å. Molecular modeling using known bond lengths for biphenyl[26] and standard bond lengths and bond angles and assuming full extension of the 3′-(aryloxy)propyl spacer shows the polymer sample to have either significant interdigitation or a large tilt angle (Figure 11B). The presence of a highly tilted mesogenic layer, along with the diffuse peak near 5.2 Å, and the observation of a schlieren texture under cross polarizers are consistent with the assignment of the mesogenic phase as being a smectic phase.[2,12,22] The sharp high-angle spacing at 3.3 Å may result from stacking of the aromatic biphenyl groups. Such alignment in biphenyl crystals is well known.[26,27]

The linear dependence of T_g on side chain length (or bulk) and the observations of liquid crystalline behavior in the poly(1-methyl-1-sila-*cis*-pent-3-enes) may be due to ordering of the pendant groups separate from that of the main chain. As the length of the side chain increases, calculated using known bond lengths and bond angles (Figure 3), from poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) with a length of 1.5 Å for the methyl group to VII with a length of 15.5 Å for the (biphenylyloxy)propyl group, the pendant groups should have a better ability to align. This ordering of the side chain would then have greater influence upon the bulk order in the system. Such relationships are well known for side chain liquid crystalline polymers, although they have previously been discussed in terms of alkyl spacer length or the size of the mesogen.[3,4,11,21]

An alternative method for the preparation of these polymers would be to graft the allyl aryl ethers onto the backbone of poly(1-methyl-1-sila-*cis*-pent-3-ene) or poly(1-phenyl-1-sila-*cis*-pent-3-ene) via platinum-catalyzed hydrosilation reactions. This would lead to low molecular weight material due to low molecular weights of the starting polymers.[14,15] Furthermore, cross-linking of the materials is possible due to the Pt-catalyzed reaction of Si–H with adventitious water.[28,29] Despite these limitations, low molecular weight VI was prepared in this way. No cross-linking of the material was noted from GPC or NMR analysis. This material permits us to compare the properties of high and low molecular weight VI.

High molecular weight VI has a T_g of −31 °C while low molecular weight VI (M_n a factor of 100 smaller) has a T_g of −29 °C. The small difference in the T_g may be due to the presence of end groups in the low molecular weight VI. The end groups of poly(1-methyl-sila-*cis*-pent-3-ene) are 1-methyl-1-silacyclopent-3-enes.[14] These conformationally inflexible rings would be expected to increase the T_g of low molecular weight VI. However, the difference in T_g is surprising since it is known that linear lower molecular weight polymers have lower T_gs.[21] The onset of thermal decomposition of high molecular weight VI (412 °C) is 30 degrees higher than that of low molecular weight VI. Such differences in thermal stability due to molecular weight have been observed for other poly(1-sila-*cis*-pent-3-enes).[17,30]

High molecular weight VI, VII, VIII, IX, and X are the most thermally stable poly(1-sila-*cis*-pent-3-enes) yet prepared, having onset temperatures between 412 and 430 °C. These systems have highly polarizable aryloxy pendant groups which apparently control the order of these materials in the bulk state. Poly(1-sila-*cis*-pent-3-enes) without the aryloxy groups have lower thermal stabilities; for instance, poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene), with similar M_w/M_n to the polymers prepared here, has an onset of thermal decomposition of 380 °C.[17] In addition, poly(1-sila-*cis*-pent-3-enes) prepared without the aryloxy groups have not shown liquid crystalline phase formation.

Summary

Unsaturated carbosilane polymer backbones such as that of poly(1-methyl-1-sila-*cis*-pent-3-ene) or poly(1-phenyl-1-sila-*cis*-pent-3-ene) can be used as stable platforms for the attachment of mesogenic side chains. Mesogen-substituted monomers may be conveniently prepared and polymerized if no incompatibility between the mesogen and the anionic initiator exists. This then guarantees 100% substitution of the desired mesogen in the polymer. However, it has been demonstrated that postpolymerization hydrosilation grafting of alkene to reactive Si–H substituted carbosilane polymers is also viable. The formation of liquid crystalline materials from the appropriate mesogenic groups has been shown.

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