Synthesis and Properties of Ethynylene–Disilanylene Copolymers

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ABSTRACT: Alternating copolymers, $(\text{-SiR}_2\text{SiR}_2\text{C}{\equiv}\text{C})$-, were synthesized in high yields from 1,2-dichlorodisilanes and dilithium reagents of 1,2-diethynyldisilanes ($\text{HC}{\equiv}\text{CSiR}_2\text{SiR}_2\text{C}{\equiv}\text{CH}$). The polymers show UV absorption maxima at ~240 nm indicative of Si–Si σ–π conjugation and sharp ^{1}H and ^{13}C NMR spectra suggesting that the polymers exist in a single conformation.

Introduction

Electron delocalization between Si–Si σ bonds and π systems has been conclusively established in various polysilane compounds containing unsaturated or aromatic groups.[1] Disilanes bearing substituents with π-electron systems generally show absorption maxima (λ_{max}) at longer wavelength than for hexaalkyldisilanes (Table I). This red shift is attributed to σ–π conjugation involving the Si–Si σ and C=C π^* orbitals.[2,3] Examples of Si–Si σ–π electron delocalization in polymeric systems are however relatively few.[7] We now wish to report syntheses and properties of a new Si–Si σ–π polymeric system, the ethynylene–disilanylene alternating copolymers.

Results and Discussion

Ethynylene–disilanylene copolymers were prepared as shown in Scheme I. The acetylenic hydrogens of 1,2-diethynyldisilanes were deprotonated by *n*-butyllithium to form dilithium species **4**. These lithium compounds are soluble in THF and can be reacted with 1,2-dichlorodisilanes to form the ethynylene–disilanylene copolymers in high yields.

In place of *n*-butyllithium, Grignard reagents such as ethylmagnesium bromide can be used for the metalation of 1,2-diethynyldisilanes. The di-Grignard reagent so formed also reacts with 1,2-dichlorodisilanes to give copolymers. In this case, however, a relatively concentrated (>0.5 M) THF solution of the dimagnesium compound has to be used so that the chain extending polymerization is favored over a cyclization reaction.[8]

Table II shows properties of the polymers obtained by these methods. Molecular weights range from a few thousand to fifteen thousand, relative to polystyrene standards; a typical GPC result for **1a** is shown in Figure 1. Molecular weight distribution are monomodal but become broader as the molecular weights increase. Polymer **1a** with methyl substitution only on silicon is a white solid with a relatively high melting point, poorly soluble in organic solvents; polymer **1b** with *n*-butyl groups on silicon is a white sticky solid with a relatively low melting point. Compound **1b** is very soluble in organic solvents and readily forms flexible films. The infrared spectra of all of the polymers show bands near 3300 and 1050 cm^{-1}, assigned to $-\text{C}{\equiv}\text{CH}$ and –SiOSi vibrations, respectively. However these bands are quite weak, indicating that only small amounts of these moieties are present.

All of the polymers show UV absorption maxima near 240 nm, indicative of Si–Si σ–π conjugation. Moreover these λ_{max} values are longer by 10–20 nm than those of the model compounds in Table I, indicating that σ–π delocalization is more extensive in the polymers than in analogous monomeric compounds.

Scheme I
Synthesis of Ethynylene–Disilanylene Copolymers

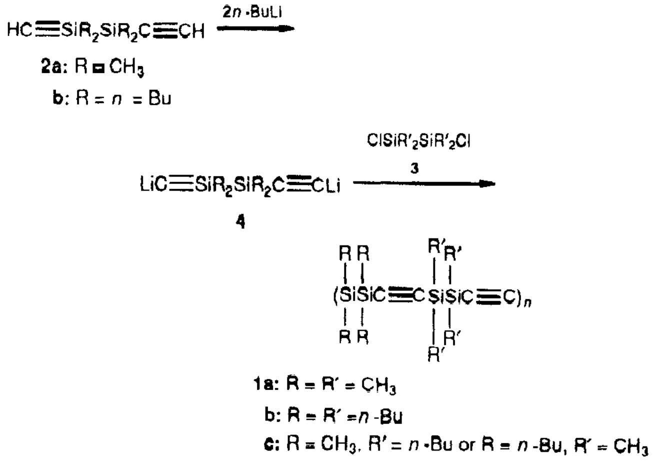

Table I
UV Absorption Maxima of Si–Si σ–π Electron-Delocalized Compounds

compound	λ_{max}, nm	ref
$\text{Me}_3\text{SiSiMe}_3$	197–200	4
$\text{PhMe}_2\text{SiSiMe}_3$	231	5
$\text{HC}{\equiv}\text{CSiMe}_2\text{SiMe}_2\text{C}{\equiv}\text{CH}$	217	*a*
$\text{Me}_3\text{SiC}{\equiv}\text{CSiMe}_2\text{SiMe}_2\text{C}{\equiv}\text{CSiMe}_3$	223, 230	6

[a] This work; see the Experimental Section.

Table II
Properties of Disilanyleneacetylene Polymers

compd	appearance	mp, °C	UV, nm	M_w	M_n	$\bar{M}_w/M_n$
1a	white solid	140–157	234, 240	4600	2900	1.6
1a[a]	white solid	166–180	232, 239	10 000	7000	1.4
1b	white sticky solid	60–70	210, 243	14 800	3400	4.4
1b[b]	white sticky solid	64–70	213, 244	10 700	3700	2.9
1c	clear viscous liquid		215 (sh), 227, 239 (sh)	3400	1300	2.6

[a] Polymer obtained from di-Grignard reagent **2a** with dichlorodisilane **3a** in concentrated THF solution. [b] Reprecipitated from THF/EtOH.

Typical polysilane polymers exhibit very broad resonances in the ^{1}H and ^{13}C NMR spectrum, due to the many proton and carbon environments resulting from numerous different conformations of the polysilane chain. The ethynylene–disilanylene copolymers, however, show only narrow lines in the ^{1}H and ^{13}C NMR, broadened

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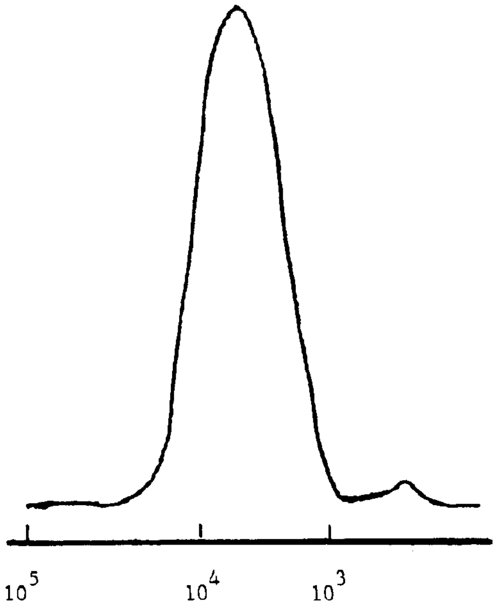

Figure 1. GPC curve for polymer **1a**. $\bar{M}_w$ values are relative to polystyrene standards.

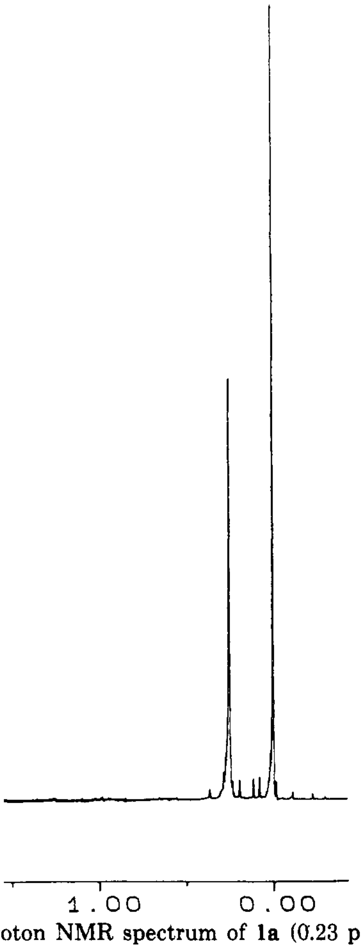

Figure 2. Proton NMR spectrum of **1a** (0.23 ppm) and tetramethylsilane (0.00 ppm), showing the narrow resonance for the methyl groups in the polymer.

only slightly compared with those for their monomeric precursors. As shown in Figure 2, the major proton resonance for **1a** is only about twice as broad as that for tetramethylsilane. Decreasing the temperature to −30 °C leads only to some viscosity broadening, which affects the **1a** and tetramethylsilane resonances equally. The ^{13}C NMR spectra also show very narrow lines, as displayed in Figure 3 for **1b**, which are likewise only slightly broadened by viscosity effects at lower temperatures.

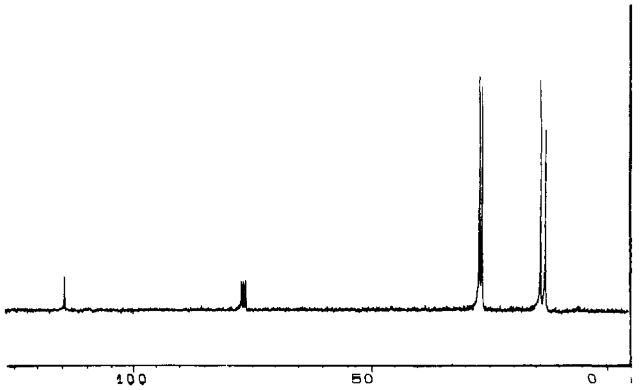

Figure 3. Carbon-13 NMR spectrum for **1b**, showing narrow resonances for the carbon atoms of the polymer.

If the narrow resonances for these polymers resulted from chain mobility leading to averaging of conformations, significant broadening would be expected as the temperature is decreased. Since this is not observed, we infer that the number of proton environments in these polymers must be very limited, perhaps because the polymers show a strong preference for a single conformation. This could either be rodlike, with trans torsional angles at the Si–Si bonds, or helically coiled, with cis junctions at silicon. Further studies of these new polymers will be necessary to elucidate their conformational structure.

Experimental Section

General Data. All reactions unless otherwise noted were carried out under an atmosphere of dry nitrogen or argon. Solvents were dried over sodium/benzophenone and distilled just before use. All glassware was thoroughly dried in an oven at 110–120 °C.

Proton NMR spectra were recorded on a Bruker WP-200SY FT spectrometer; UV spectra were determined for THF solutions on a Perkin-Elmer Lamda Array 3840 UV/vis spectrophotometer; a Polaris FT-IR spectrometer was used for IR spectra. Mass spectra and exact mass determinations were performed on a Kratos MS-80 mass spectrometer at 30 eV. GC/MS was carried out on a Carlo Erba 4160 gas chromatograph system using a 30 m × 0.36 mm i.d. fused silica capillary column coated with 5% phenylmethylsilicone.

A Hewlett-Packard 5890 gas chromatography with a flame ionization detector, a 10 m × 0.56 mm i.d. megabore column coated with 5% phenylmethylsilicone, and HP 3390A integrating recorder was used for analytical gas chromatography. Preparative gas chromatography was performed on a Gow Mac Model 550P gas chromatograph using a thermal conductivity detector (TCD) and helium as the carrier gas. Normally, a 6 ft × 0.25 in. column packed with 5% SE-30 adsorbed on Chromosorb-W was used. Melting and boiling points reported here are uncorrected. Molecular weights of polymers were determined with four microstyragel columns, using THF as the eluent, and are relative to polystyrene standards.

Phenyldi-*n*-butylchlorosilane (5). A 500-mL three-necked round-bottom flask was equipped with a motor-driven stirrer, 250-mL pressure-equalized dropping funnel, and gas inlet. Phenyltrichlorosilane (30 mL, 0.188 mol) and 100 mL of dry THF were placed in the flask, and 250 mL of 1.5 M *n*-butyllithium hexane solution (0.375 mol) was added dropwise with stirring over 7.5 h at −78 °C. The mixture was filtered to remove lithium chloride, and the salt was washed with dry hexane. The solvents were stripped, leaving a pale yellow viscous liquid and small amount of salt. The organic material was redissolved in hexane and refiltered, and the salt was washed with a small portion of dry hexane. The filtrate was pumped off and distilled under vacuum to give 40.2 g of distillate [bp 95–140 °C (mainly 100–109 °C) (0.5 Torr)]. GC analysis showed that it contained 1.4% of $PhSi(n\text{-}Bu)Cl_2$, 84.2% of $PhSi(n\text{-}Bu)_2Cl$, and 13.7% of $PhSi(n\text{-}Bu)_3$. The yield of the $Ph(n\text{-}Bu)_2SiCl$ based on the $PhSiCl_3$ employed was 84%. GCMS (30 eV) *m/e* (relative intensity): first peak, $\mathrm{PhSi(}n\mathrm{\text{-}Bu)Cl_2}$, 236 ($\mathrm{M^+}$ + 4, 0.6), 234 (M + 2, 3.7), 232 ($\mathrm{M^+}$, 5.2), 175 ($\mathrm{M^+}$ – *n*-Bu, 100), 154 (49), 113 (40), 78 (79); second peak, $\mathrm{PhSi(}n\mathrm{\text{-}Bu)_2Cl}$, 256 ($\mathrm{M^+}$ + 2, 0.06), 254 ($\mathrm{M^+}$, 0.16), 197 ($\mathrm{M^+}$ – *n*-Bu, 53), 176 (26), 141 (100), 119 (17); third peak, $\mathrm{PhSi(}n\mathrm{\text{-}Bu)_3}$, 219 ($\mathrm{M^+}$ – *n*-Bu, 49), 163 (100), 121 (31), 107 (76), 85 (23).

1,2-Diphenyl-1,1,2,2-tetra-*n*-butyldisilane (6). Lithium wire (1.45 g, 0.21 mol, Aldrich) was quickly cut into small pieces and added to 100 mL of dry THF in a 250-mL Schlenk flask. A 125-mL pressure-equalized addition funnel was attached, and the system was purged with dry argon. The chlorosilane mixture (60 g, 84.2% $\mathrm{Ph(}n\mathrm{\text{-}Bu)_2SiCl}$) was added dropwise over 2.5 h at 0 °C. The reaction mixture was then stirred overnight at 0 °C to room temperature. The THF was pumped off, and 50 mL of hexane was added to the mixture, which was filtered to remove the lithium chloride and unreacted lithium. The solids were washed with 50 mL of hexane, and the combined filtrate was poured into an aqueous buffer solution to give a yellow organic layer, which was separated and extracted with 30 mL of hexane. The combined organic layer was washed with 1 N HCl (50 mL × 2) and with water (50 mL × 2) and dried over $\mathrm{CaCl_2}$. The solution was filtered and evaporated; fractional distillation gave 36.9 g (85%) of $\mathrm{(Ph(}n\mathrm{\text{-}Bu)_2Si)_2}$ as a colorless viscous liquid, bp 177–185° (0.16 Torr). The liquid later solidified to give colorless crystals: mp 38–40 °C; ^{1}H NMR (200 MHz, $\mathrm{CD_2Cl_2}$) δ 0.66–1.02 (m, 10 H, $\mathrm{SiC}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_3$), 1.10–1.44 (m, 8 H, $\mathrm{SiCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$, 7.16–7.41 (m, 10 H, $\mathrm{C_6}\mathit{H}_5$; MS (30 eV), *m/e* (rel intensity) 438 ($\mathrm{M^+}$, 18), 381 ($\mathrm{M^+}$ – *n*-Bu, 3), 325 (10), 269 (67), 219 (67), 163 (100), 107 (62); exact mass determination calcd for $\mathrm{C_{28}H_{46}Si_2}$ 438.3138, measd 438.3131.

1,2-Dichloro-1,1,2,2-tetra-*n*-butyldisilane (3b). A 500-mL three-necked round-bottom flask was set up with a magnetic stirrer tip, a reflux condenser, gas inlet, septum cap, and a glass stopper. $\mathrm{PhSi(}n\mathrm{\text{-}Bu)_2Si(}n\mathrm{\text{-}Bu)_2Ph}$ (34.6 g, 78.9 mmol), 150 mL of dry benzene, and 0.172 g of anhydrous $\mathrm{AlCl_3}$ were placed in the flask. Dry HCl gas was introduced into the reaction flask through the septum cap at room temperature. An exothermic reaction immediately occurred. After the exotherm subsided (15–20 min), 5 mL of acetone (dried over $\mathrm{CaCl_2}$ and filtered) was added to the flask to deactivate the $\mathrm{AlCl_3}$. Benzene was distilled out under reduced pressure (25–30 mmHg). After simple distillation of the residual material, fractional distillation under vacuum gave 24.7 g (88%) of $\mathrm{ClSi(}n\mathrm{\text{-}Bu)_2Si(}n\mathrm{\text{-}Bu)_2Cl}$: bp 115–118 °C (0.15 Torr); ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 0.66–1.10 (m, 5 H, $\mathrm{SiC}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_3$), 1.23–1.55 (m, 4 H, $\mathrm{SiCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$); MS (30 eV), *m/e* (rel intensity) 358 ($\mathrm{M^+}$ + 4, 0.6), 357 ($\mathrm{M^+}$ + 3, 0.6), 356 ($\mathrm{M^+}$ + 2, 2.8), 355 ($\mathrm{M^+}$ + 1, 1.0), 354 ($\mathrm{M^+}$, 3.6), 297 ($\mathrm{M^+}$ – *n*-Bu, 3.9), 177 (39), 142 (52), 114 (100), 86 (71); exact mass determination calcd for $\mathrm{C_{16}H_{36}Cl_2Si_2}$ 354.1732, measd 354.1722.

1,2-Diethynyl-1,1,2,2-tetra-*n*-butyldisilane (2b). A 250-mL three-necked round-bottom flask was equipped with a reflux condenser, a 125-mL pressure equalized dropping funnel, a gas inlet, and a magnetic stirrer bar. In the flask was placed 250 mL of 0.67 M ethynylmagnesium bromide in THF (100 mmol), prepared from acetylene gas and ethylmagnesium bromide in THF according to the established method. To the ethynylmagnesium bromide was added 15 g (42.3 mmol) of $\mathrm{ClSi(}n\mathrm{\text{-}Bu)_2Si(}n\mathrm{\text{-}Bu)_2Cl}$ in 20 mL of THF over 15 min at room temperature. After completion of addition, the mixture was heated to reflux for 3 h. After cooling, 25 mL of hexane was added followed by 25 mL of 1 N aqueous HCl with external cooling. The reddish brown organic layer was separated and washed 12 times with 25 mL of 1 N HCl. The combined aqueous layer was extracted with 10 mL of hexane three times. The combined organic layer was washed with 25 mL of 1 N HCl six times. (These procedures are necessary to remove as much THF as possible from the organic layer.) The hexane solution was dried over $\mathrm{MgSO_4}$, filtered, and evaporated. The residual yellow liquid was distilled under vacuum to give 13.2 (93%) of colorless liquid **2b**: bp 112–119 °C (0.45 Torr); ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 0.59–0.96 (m, 10 H, $\mathrm{SiC}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_3$), 1.20–1.51 (m, 8 H, $\mathrm{SiCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.46 (s, 2 H, $\mathrm{SiC{\equiv}C}\mathit{H}$); UV (solution in THF) $\lambda_{\max}$ 222 nm; IR (neat sample between KBr plates, $\mathrm{cm^{-1}}$) 3290 (s, $-\mathrm{C{\equiv}}\mathit{CH}$), 2950 (s), 2920 (s), 2870 (s), 2025 (s, $-\mathit{C}{\equiv}\mathit{C}-$), 1470 (s), 1080 (s), 880 (m), 670 (s); MS (30 eV), *m/e* (rel intensity) 334 ($\mathrm{M^+}$, 0.7), 277 ($\mathrm{M^+}$ – *n*-Bu, 12), 221 (72), 165 (100), 109 (52); exact mass determination calcd for $\mathrm{C_{20}H_{38}Si_2}$ 334.2512, measd 334.2511. Anal. Calcd for $\mathrm{C_{20}H_{38}Si_2}$: C, 71.77; H, 11.44. Found: C, 72.19; H, 11.41.

1,2-Dichloro-1,1,2,2-tetramethyldisilane (3a). Compound **3a** was prepared from hexamethyldisilane, aluminum chloride and acetyl chloride in 90% yield according to the method of Sakurai et al.[9]

1,2-Diethynyl-1,1,2,2-tetramethyldisilane (2a). Following the published procedure,[10] compound **2a** was obtained from the reaction of 1,2-dichloro-1,1,2,2-tetramethyldisilane with ethynylmagnesium bromide in THF in good yield (70–80%). UV: $\lambda_{\max}$ 217 nm (THF solution).

Synthesis of the Copolymer 1a with *n*-BuLi. 1,2-Ethynyl-1,1,2,2-tetramethyldisilane (1.0 g, 6.0 mmol) was treated with 5.1 mL (12.7 mmol) of 2.5 M *n*-BuLi in hexane, (Aldrich Chemical Co.) in 30 mL of dry THF (distilled from sodium benzophenone ketyl) at room temperature under $\mathrm{N_2}$ atmosphere for 4 h to form the dilithium reagent ($\mathrm{LiC{\equiv}CSi(CH_3)_2Si(CH_3)_2\text{-}C{\equiv}CLi}$). The dilithium reagent was treated with 1.13 g (6.0 mmol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane [$\mathrm{Cl(CH_3)_2\text{-}SiSi(CH_3)_2Cl}$]in 2 mL of THF and refluxed overnight under $\mathrm{N_2}$ atmosphere. The solvent was pumped off to leave a pale yellow viscous wax. It was dissolved in 150 mL of chloroform, washed with aqueous ammonium chloride solution (50 mL × 2) and then with 50 mL of water, and dried over $\mathrm{CaCl_2}$. The solution was filtered, evaporated, and dried under vacuum to leave about 1.4 g (87%) of the crude polymer **1a** as slightly sticky solid.

The polymer was purified by reprecipitation from chloroform–isopropyl alcohol: mp 140–157 °C; ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 0.06, 0.10, 0.17, 0.23 ($\mathrm{SiC}\mathit{H}_3$), all singlets (the relative intensity of the peak at 0.23 ppm is >90% of the total); ^{13}C NMR (200 MHz, $\mathrm{CDCl_3}$) δ –3.49 ($\mathrm{Si}\mathit{C}\mathrm{H_3}$), 114.55 ($\mathit{C}{\equiv}\mathrm{C}$), both sharp singlets; IR (KBr disk, $\mathrm{cm^{-1}}$) 2950 (s), 2920 (m), 2890 (m), 2140 (vw), 2090 (vw), 1415 (m), 1405 (m), 1245 (vs). Anal. Calcd for $\mathrm{(C_6H_{12}Si_2)_{\mathit{n}}}$: C, 51.35; H, 8.62. Found: C, 50.86; H, 8.87.

Synthesis of the Copolymer 1a with EtMgBr. 1,2-Ethynyl-1,1,2,2-tetramethyldisilane (1.0 g, 6.0 mmol) was treated with 6.3 mL (12.6 mmol) of 2.0 M EtMgBr in THF solution (Aldrich Chemcial Co.) in 8 mL of dry THF at room temperature for 1.5 h to form the magnesium compound $\mathrm{BrMg\text{-}C{\equiv}CSi(CH_3)_2Si(CH_3)_2C{\equiv}CMgBr}$. The solution containing the di-Grignard reagent was then treated with 1.13 g (6.01 mmol) of $\mathrm{Cl(CH_3)_2SiSi(CH_3)_2Cl}$ in 1.5 mL of THF at room temperature overnight. The THF was pumped off to leave a white solid, which was washed with water (20 mL × 3) and then ethanol (20 mL × 2) and dried under vacuum to leave about 1.3 g (81%) of the crude polymer **1a** as a white solid. The polymer was purified by reprecipitation from chloroform–isopropyl alcohol, mp 166–180 °C.

Synthesis of the Copolymer 1b. 1,2-Diethynyl-1,1,2,2-tetra-*n*-butyldisilane (1.0 g, 2.9 mmol) was treated with 3.75 mL (6.0 mmol) of 1.6 M *n*-BuLi hexane solution in 20 mL of dry THF at room temperature for 2 h to form the dilithium reagent, to which was added 1.05 g (2.8 mmole of $\mathrm{Cl(}n\mathrm{\text{-}Bu_2Si)_2Cl}$ in 3 mL of THF. The mixture was stirred at room temperature overnight, and then the solvent was evaporated from the reaction mixture. To the residue was added 50 mL of hexane, and the solution was washed with 20 mL of aqueous $\mathrm{NH_4Cl}$ (30 mL × 2) and then with water (30 mL × 1) and dried over $\mathrm{CaCl_2}$. The solution was filtered, evaporated, and dried under vacuum yielding 1.3 g (73%) of the crude polymer as a pale yellow sticky solid. The polymer was purified by reprecipitation from THF/ethanol: mp 64–70 °C; ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 0.60–0.78 ($\mathrm{SiC}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$, t), 0.78–0.95 ($\mathrm{SiCH_2CH_2CH_2C}\mathit{H}_3$), 1.20–1.51 ($\mathrm{SiCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$, m); ^{13}C NMR (200 MHz, $\mathrm{CDCl_3}$) δ 12.77, 13.60, 26.57, 27.02, 144.54 ($\mathrm{C{\equiv}C}$), all sharp singlets; IR (KBr disk) 2950 (vs), 2910 (vs), 2870 (vs), 2860 (vs), 1460 (s), 1370 (m), 1180 (m), 1170 (m), 1075 (s), 1025 (m), 960 (m), 880 (m), 870 (m), 775 (s), 760 (s). Anal. Calcd for $\mathrm{(C_{18}H_{36}Si_2)_{\mathit{n}}}$: C, 70.05; H, 11.76; Si, 18.20. Found: C, 69.38; H, 11.77; Si, 18.00.

Synthesis of the Copolymer 1c. The dilithium reagent was prepared from 0.48 g (2.9 mmol) of $\mathrm{HC{\equiv}CSiMe_2SiMe_2C{\equiv}CH}$ and 3.65 mL (5.84 mmol) of 1.6 M *n*-BuLi in hexane, in 20 mL of dry THF as described above. To the dilithium reagent was

Macromolecules **1990**, *23*, 1301-1308 **1301**

added 1.0 g (2.8 mmol) of $Cl(n\text{-}Bu)_2SiSi(n\text{-}Bu)_2Cl$ in 5 mL of dry THF, and the solution was refluxed for 22 h. After the usual workup, 1.34 g of crude polymer was obtained as clear viscous liquid.

In an alternate synthesis, the dilithium reagent was prepared from 0.97 g (2.9 mmol) of $HC\equiv CSi(n\text{-}Bu)_2Si(n\text{-}Bu)_2C\equiv CH$ and 3.65 mL (5.84 mmol) of 1.6 M *n*-BuLi hexane solution, in 20 mL of dry THF. To the dilithium reagent was added 0.52 g (2.8 mmol) of $ClMe_2SiSiMe_2Cl$ in 5 mL of dry THF, and the solution was refluxed for 22 h. After the ususal workup, 1.12 g of crude polymer was obtained as a clear viscous ligand. UV: λ_{max} 214 (sh), 226, 240 (sh) nm (THF solution).

Note Added in Proof. A recent communication reports the synthesis of polymers similar to these by ring opening of the 8-membered ring dimer: Ishikawa, M.; Hasegawa, Y.; Hatana, T.; Kunai, A. *Organometallics* **1989**, *8*, 2741. We have also observed ring-opening polymerization and will report it later.

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(8) The reaction of the di-Grignard reagents with 1,2-dichlorodisilanes in dilute (0.1 M) THF solution led to the formation of the eight-membered ring disilanyleneacetylene. See: Iwahara, T.; West, R. *J. Chem. Soc., Chem. Commun.* **1988**, *14*, 954.

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Registry No. **1a** (SRU), 123438-63-1; **1b** (copolymer), 124755-68-6; **1b** (SRU), 124755-60-8; **1c** (copolymer), 124755-69-7; **1c** (SRU), 124755-61-9; **2b**, 124755-59-5; **3b**, 122202-74-8; **5**, 114953-59-2; **6**, 124755-58-4; $PhSi(Cl)_3$, 98-13-5; *n*-BuLi, 109-72-8; $PhSi(n\text{-}Bu)Cl_2$, 17887-42-2; $PhSi(n\text{-}Bu)_3$, 18510-29-7; $HC\equiv CMgBr$, 4301-14-8; $(LiC\equiv C(Si(Me)_2)_2C\equiv CLi)(Cl(Si(Me)_2)_2Cl)$ (copolymer), 124755-64-2; $(BrC\equiv C(Si(Me)_2)_2C\equiv CBr)(Cl(Si(Me)_2)_2Cl)$ (copolymer), 124755-66-4.

Normal-Mode Analysis of Infrared and Raman Spectra of Crystalline Isotactic Poly(methyl methacrylate)

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ABSTRACT: Infrared spectra of oriented and Raman spectra of nonoriented samples of crystalline isotactic poly(methyl methacrylate) (i-PMMA) have been measured. These vibrational spectra have been analyzed by means of normal-mode calculations, using a combined valence force field transferred without refinement from hydrocarbons and from methyl acetate. Calculations have been done for single chain 5/1 and 10/1 helical backbone conformations. Best agreement in the low-frequency region is found between the observed and calculated frequencies for the 10/1 structure. Infrared and Raman bands over the entire spectral region can be satisfactorily interpreted on the basis of the potential energy distributions and dispersion curves for the 10/1 helical conformation of the single i-PMMA chain in the double-stranded structure.

Introduction

Infrared and Raman spectroscopy, in combination with normal mode calculations, provide a powerful tool for structural analyses of polymers. We present here such a study of the structure and spectrum of isotactic poly(methyl methacrylate) (i-PMMA).

There have been several reports of infrared and Raman spectra and tentative band assignments for (i-PMMA).[1-11] Differently deuterated i-PMMA samples were used in the analyses of the C–H stretch and bend modes.[2,6,7] Bands exhibiting temperature dependences in the infrared spectra of i-PMMA in bulk and in solution were assigned to various conformational forms.[3,8,9] Characteristic solid-state infrared bands of the crystalline and the amorphous phases were determined.[10,11] Using a Urey–Bradley force field refined for polyesters, normal-mode calculations of the low-frequency skeletal modes have been performed on 5/1 helical chain models of i-PMMA.[5] How-

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