Copolymerization of 1,1-Dimethyl-1-silacyclopent-3-ene and 1,1-Diphenyl-1-silacyclopent-3-ene. Characterization of Copolymer Microstructures by ^{1}H, ^{13}C, and ^{29}Si NMR Spectroscopy

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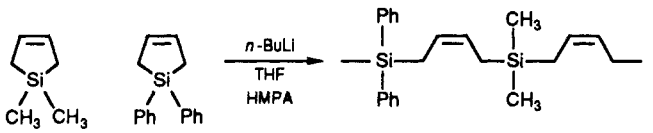
ABSTRACT: 1,1-Dimethyl-1-silacyclopent-3-ene and 1,1-diphenyl-1-silacyclopent-3-ene have been copolymerized by treatment with *n*-butyllithium and hexamethylphosphoramide in THF at −50 °C. Random copolymers are formed. The microstructures of these have been characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. Thermal stabilities of these copolymers have been determined by thermogravimetric analysis. Their glass transition temperatures have been measured by differential scanning calorimetry.

There is considerable interest in synthesis of copolymers since variation in the composition of these can affect copolymer properties.[1] Ethylene/propylene copolymers have, in particular, been thoroughly studied.[2] We have previously reported that 1,1-dimethyl-1-silacyclopent-3-ene (I) undergoes anionic ring-opening polymerization to yield poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (II) while under similar conditions 1,1-diphenyl-1-silacyclopent-3-ene (III) yields poly(1,1-diphenyl-1-sila-*cis*-pent-3-ene) (IV).[3] We should like to report that treatment of mixtures of I and II in THF solvent at −50 °C with catalytic amounts of *n*-butyllithium and hexamethylphosphoramide (HMPA) yields random copolymers of approximately equal molecular weight whose composition depends on the initial molar ratio of I and II as well as on the percent of the monomer mixture converted to copolymer (see Table I).



The ratio of 1,1-dimethyl-1-sila-*cis*-pent-3-ene (V) units to 1,1-diphenyl-1-sila-*cis*-pent-3-ene (VI) units in the copolymers was determined by integration of the ^{1}H and ^{29}Si NMR spectra. Comparison of the ^{1}H NMR integration of the methyl signals (V) to the phenyl signals (VI) gives the ratio of V to VI units in the copolymers. Similarly, integration of the ^{29}Si NMR signals assigned to dimethylsilylene groups between 2.30 and 2.58 ppm compared to those assigned to diphenylsilylene groups between −10.55 and −10.38 ppm permits determination of the ratio of V to VI groups in the copolymers. ^{1}H and ^{29}Si NMR integration gave consistent values.

The ^{1}H NMR of V units is sensitive to copolymer microstructure. The protons of the methyl groups bonded to silicon give rise to three peaks at 0.01, −0.02, and −0.05 ppm. These can be assigned on the basis of a triad analysis. The peak at 0.01 ppm is assigned to the triad in which V units are found on both sides of the central V unit. The second peak at −0.02 ppm is assigned to the triad in which a V unit is on one side of the central V unit while a VI unit is on the other side. Finally, the small peak at −0.05 ppm is assigned to the triad in which VI units are on both sides of the central V unit. The intensity of these peaks varies with the ratio of V to VI units in the copolymers. When the ratio of V/VI increases, the relative intensity of the peak at 0.01 ppm increases while the intensity of the peak at −0.05 ppm decreases. When V/VI > 1, the peak at −0.05 ppm can hardly be seen. The peak centered at 1.45 ppm is assigned to the protons of methylene groups adjacent to dimethylsilylene groups. The chemical shift of these protons is not sensitive to copolymer microstructure. The broad peak at 1.8 ppm is assigned to methylene groups adjacent to diphenylsilylene groups whose nearest neighbor is a diphenylsilylene group, while the broad peak at 2.0 ppm is assigned to methylene groups adjacent to diphenylsilylene groups whose nearest neighbor is a dimethylsilylene group. The signal at 5.30 ppm is assigned to the vinyl proton resonances of both V and VI units. Finally, the resonances between 7.6 and 7.2 ppm are assigned to the phenyl groups of VI units. These are not sensitive to polymer microstructure (see Figure 1).

^{13}C NMR data of the copolymers can, likewise, be accounted for by a triad microstructure analysis. Three distinct dimethylsilylene-centered triads as well as three distinct diphenylsilylene-centered triads are predicted. The ^{13}C resonances observed have been assigned by comparison with those observed for II and IV (see Figure 2). This provides strong evidence that the cis configuration of the carbon–carbon double bonds has been retained during the copolymerization of I and III.[3,4]

Three distinct methyl ^{13}C resonances which can be assigned to dimethylsilylene-centered triads are observed at −3.47, −3.51, and −3.54 ppm. The peak at −3.47 ppm is assigned to the triad in which V units are found on both side of the central V unit. The second peak at −3.51 ppm is assigned to the triad in which a V unit is on one side of the central V unit while a VI unit is on the other side. Finally, the peak at −3.54 ppm is assigned to the triad in which VI units are on both sides of the central V unit. The peak at −3.54 ppm can be seen clearly in the spectrum of the copolymer in which the ratio of V/VI is equal to 1/3.1. In the spectrum of copolymers in which the ratio of V/VI is larger, this peak becomes smaller or disappears. Each of the symmetric triads gives rise to a single vinyl ^{13}C resonance while the unsymmetrical triad gives rise to two vinyl ^{13}C signals. In fact, four res-

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Table I
Copolymerization of I and III

molar ratio of monomers I/III	ratio of V/VI in copolymer	copolymer, yield, %	M_w/M_n	T_g, °C	M_p, °C
0.0/1.0	0.0/1.0	90	8000/4400	18	130–136
1.0/1.0	1.0/3.1	28	10 650/6480	−9	107–110
3.0/1.0	1.4/1.0	40	11 500/6900	−26	<25
2.8/1.0	1.9/1.0	51	9850/5400	−32	<25
8.3/1.0	2.9/1.0	31	10 700/6700	−44	<25
1.0/0.0	1.0/0.0	93	117 400/47 200	−64	<25

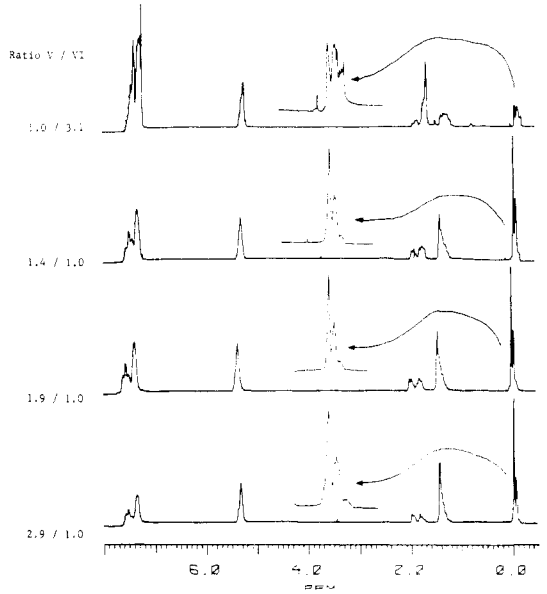

Figure 1. ^{1}H NMR spectra of copolymers.

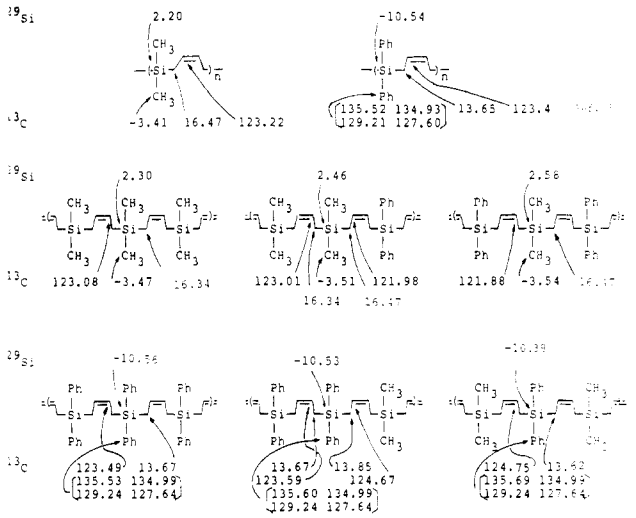

Figure 2. Assignments of ^{13}C and ^{29}Si NMR chemical shifts of copolymer microstructures.

onances are observed at 123.08, 123.01, 121.96, and 121.87 ppm. The change in their relative intensities of these signals as the ratio of V to VI changes permits unambiguous peak assignments.

Three distinct diphenylsilylene-centered triads in the copolymers are likewise predicted. In fact, three ^{13}C resonances at 135.69, 135.60, and 135.53 ppm assigned to the ipso carbons of the phenyl groups are observed. However, the ^{13}C resonances due to the ortho, meta, and para carbons of the phenyl groups are not sensitive to microstructure. This probably results from the fact that they are further distant from the backbone of the copolymer chain. These are observed at 134.99, 129.24, and 127.64 ppm. Each of the symmetric triads gives rise to a single unique vinyl ^{13}C resonance while the unsymmetrical triad gives rise to two nonequivalent ^{13}C signals. In fact, four vinyl ^{13}C resonances are observed at 124.76, 124.69, 123.59, and 123.49 ppm.

Similar analysis for the methylene carbons would predict that there should be four unique resonances for the methylene carbons adjacent to the central dimethylsilylene group and four unique signals for the methylene carbons adjacent to the central diphenylsilylene group. In fact, a total of five unique signals in this region is observed. The ones found at 16.47 and 16.34 ppm are assigned to methylene groups adjacent to central dimethylsilylene units, while the ones observed at 13.85, 13.67, and 13.62 ppm are assigned to methylene adjacent to central diphenylsilylene units. The observation of five rather than eight signals can be accounted for, if some of the signals due to the unsymmetrical triads fortuitously have chemical shifts which are identical with those of the related symmetrical triads (see Figure 3). This phenomenon has been previously observed in related systems.[4]

The ^{29}Si NMR of the copolymers can also be accounted for on the basis of triad analysis. Three distinct dimethylsilylene-centered triads as well as three distinct diphenylsilylene-centered triads are predicted. In fact, two sets of three ^{29}Si NMR resonances are observed: 2.30, 2.46, and 2.58 ppm as well as −10.56, −10.53, and −10.38 ppm. The first set is assigned to dimethylsilylene-centered triads. The second set is due to diphenylsilylene-centered triads (see Figure 2). Three signals in this region are only observed in the ^{29}Si NMR spectrum of copolymers in which V/VI is less than one. These peaks merge to a single broad peak centered at −10.53 ppm in copolymers in which the ratio of V/VI is greater than one. For this reason, it has only been possible to definitely assign the resonance at −10.38 ppm to the triad in which a central VI unit has V units on either side. A decision to which of the other two triads, VI, VI, V and VI, VI, VI, the resonances at −10.56 and −10.53 ppm should be assigned is not possible. Integration of these two sets of ^{29}Si NMR resonances gives values consistent with those obtained by ^{1}H NMR integration for the ratio of V to VI units in the copolymer.

The copolymers in which the ratio of V to VI is greater than unity have similar thermal stabilities as determined by TGA. These copolymers are stable to 100 °C. Above 100 °C, they lose 1% of their original weight for every 30 °C increase in temperature to 380 °C. Rapid weight loss occurs above 380 °C. Less than 2% of the initial weight of the polymer sample remains at 450 °C (see Figure 4). On the other hand, copolymers in which the ratio of V to VI units is less than 1 are stable to 250 °C. Between 250 and 380 °C, about 10% of the initial polymer weight is lost. Rapid weight loss occurs between 380 and 450 °C.

The glass transition temperature of the copolymers which was determined by differential scanning calorimetry has been found to increase linearly with the percentage of VI units in the copolymer (see Figure 5). Such linear relationships have been previously observed.[5]

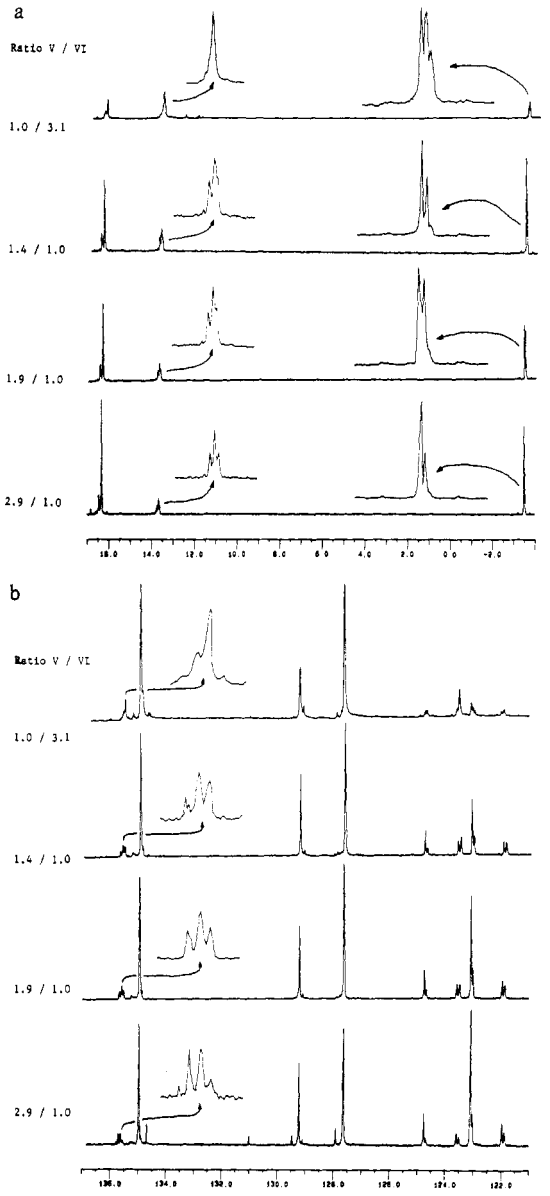

Figure 3. (a) ^{13}C NMR spectra of aliphatic region of copolymers. (b) ^{13}C NMR of vinyl and aromatic region of copolymers.

Experimental Section

^{1}H and ^{13}C NMR spectra were run on a Bruker AM-360 MHz spectrometer while ^{29}Si NMR were obtained on an IBM Bruker WP-270-SY spectrometer. ^{13}C NMR spectra were run with broad band proton decoupling. In the experiments, 10–15% solutions in chloroform-*d* were used to obtain ^{13}C and ^{29}Si NMR spectra, whereas 5% solutions were used to obtain ^{1}H spectra. Chloroform was utilized as an internal standard for ^{1}H and ^{13}C NMR spectra. All chemical shifts reported were externally referenced to TMS. A heteronuclear gated decoupling pulse sequence with a pulse delay of 25 s was used to obtained ^{29}Si NMR spectra.[6]

IR spectra were recorded on a Perkin Elmer PE-281 spectrometer. The spectra were taken of films on KBr plates.

Gel permeation chromatographic (GPC) analysis of the molecular weight distribution of the polymers was performed on a Perkin Elmer series 10 liquid chromatograph equipped with an LC-25 refractive index detector (maintained at 25 °C), a 3600 data station, and a 660 printer. A 32 cm × 77 mm Perkin Elmer PL 10-μm particle size mixed pore size cross-linked polystyrene column was used for the separation. The eluting solvent was HPLC grade THF at a flow rate of 0.7 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_P 3 600 000, 194 000, 28 000, 7600, and 2550 with M_w/M_n less than 1.09.

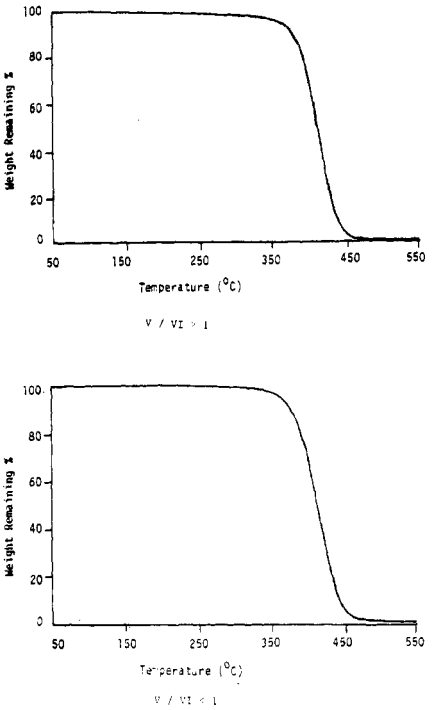

Figure 4. TGA of copolymers.

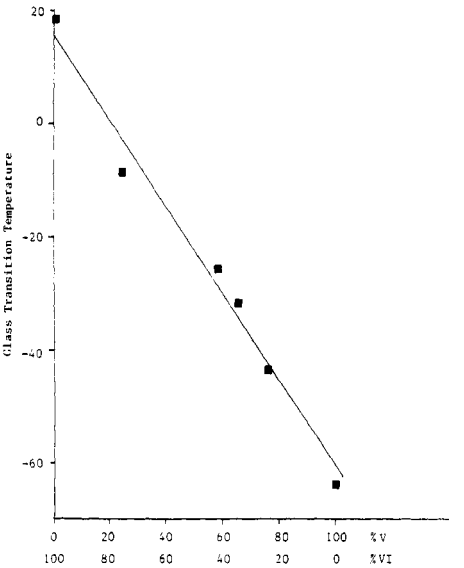

Figure 5. Dependence of glass transition temperatures on copolymer compositions.

The TGA of the copolymers was carried out on a Perkin Elmer TGS-2 instrument at a nitrogen flow rate of 40 cm^3/min. The temperature program for the analysis was 50 °C for 10 min, followed by an increase of 5 °C/min to 550 °C.

The glass transition temperatures of the copolymers were obtained on a Perkin-Elmer series 7 thermal analysis system. The temperature program was begun at −80 °C. After thermal equilibration, the temperature was increased by 20 °C/min to 20 °C. In order to obtain sharp glass transition temperatures of those copolymers which are solids, the samples were pretreated by rapid heating to 150 °C, followed by quick cooling to −50 °C. After temperature equilibrium was established, these samples were heated at 20 °C/min to 50 °C.

Gas liquid chromatography (GLPC) was carried out on a Hewlett Packard 5710A gas chromatograph equipped with a 1/8 in. × 6 ft column which was packed with 10% SE-30 on Chromosorb P.

Dimethyldichlorosilane and diphenyldichlorosilane were obtained from Petrarch Systems Inc.

THF was distilled from sodium benzophenone ketyl immediately prior to use.

n-Butyllithium was purchased from Aldrich. Its concentration was determined by double titration.[7]

HMPA was distilled from calcium hydride and stored over activated 4-Å molecular sieves.

1,1-Dimethyl-1-silacyclopent-3-ene (I) was prepared by the reaction of dimethyldichlorosilane, 1,3-butadiene, and magnesium in THF.[8,9]

1,1-Diphenyl-1-silacyclopent-3-ene (II) was prepared by the reaction of diphenyldichlorosilane, 1,3-butadiene, and magnesium in THF.[8,10]

Copolymerization of I and II was carried out under an atmosphere of argon with standard syringe–septa techniques. A 50-mL flame-dried Schlenk flask equipped with a Teflon-covered magnetic stirring bar was rinsed with 20 mL of 0.5 M *n*-butyllithium in THF. In this flask was then placed I (1.1 g, 10 mmol), II (see Table I for ratio of I to II), six drops of HMPA, and 20 mL of THF. The reaction mixture was then cooled to −50 °C. *n*-Butyllithium in hexane (10 mol % to I and II) was added with stirring. A brown color appeared immediately. The reaction mixture was kept at −50 °C for 2 h and then warmed to −10 °C. A 10-mL solution of saturated aqueous ammonium chloride was added. The aqueous layer was separated and extracted with 40 mL of ether 3 times. The combined organic layer was washed with water until the aqueous layer was neutral. The organic layer was dried over 4-Å molecular sieves. Ether was removed by evaporation under reduced pressure. The crude copolymer was dissolved in THF and was then precipitated by addition of the copolymer solution to an excess of methanol. The supernatant was found by GLPC to quantitatively contain unreacted starting monomers I and II. The copolymers were dried under vacuum for 2 days. Yields are given in Table I. All copolymers have similar IR ν: 3060, 3040, 3000, 2960, 2940, 1630, 1420, 1370, 1240, 1145, 1100, 1015 cm^{-1}.

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Registry No. (I)(II) (copolymer), 125050-22-8.

Block Copolymerization of Tetrahydrofuran with Cyclic Imino Ether: Synthesis of a New Nonionic Polymer Surfactant

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ABSTRACT: Block copolymers from tetrahydrofuran (THF) and cyclic imino ethers were synthesized in one pot by utilizing the living nature of the cationic ring-opening polymerization of both monomers. Block copolymers prepared are AB-type diblock and BAB-type triblock copolymers. The polymers had a hydrophobic poly(oxytetramethylene) segment (A block) from THF and a hydrophilic poly(*N*-acylalkylenimine) segment (B block) from the cyclic imino ether. Cyclic imino ether monomers used for construction of the hydrophilic segment are 2-methyl- and 2-ethyl-2-oxazolines and 2-methyl-5,6-dihydro-4*H*-1,3-oxazine. These block copolymers exhibit excellent surface activities and, hence, are a group of nonionic polymer surfactants. The surface activities reflected by the surface tension (γ) in water are very high. The lowest γ value reached 28.2 dyn/cm for a BAB-type triblock copolymer from THF/2-methyl-2-oxazoline.

Introduction

Cationic ring-opening polymerization of cyclic imino ethers is conveniently employed to prepare linear poly(*N*-acylalkylenimines).[1] Various block copolymers containing poly(*N*-acylalkylenimines) segments were synthesized by the polymerization of cyclic imino ethers initiated with a polymer having iodide or a *p*-toluenesulfonic acid ester group.[2] In using this initiator, the rate of initiation was slower than that of propagation and it was difficult, therefore, to control the length of poly(*N*-acylalkylenimine) segment.

Recently we have found that a poly(*N*-acylalkylenimine) becomes hydrophilic or hydrophobic by changing of the nature of the acyl group. We have paid attention to this property and synthesized a new nonionic polymer surfactant by utilizing the living nature of the cationic polymerization of cyclic imino ethers.[3] One-pot, two-stage and one-pot, three-stage copolymerizations afforded AB- and ABA- (or BAB-) type block copolymers, respec-

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