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Anionic Ring-Opening Block Copolymerization of 1,1-Dimethyl-1-silacyclopent-3-ene and 1-Methyl-1-phenyl-1-silacyclopent-3-ene

Steven J. Sargeant, Judah B. Farahi, and William P. Weber*

Donald P. and Katherine B. Loker Hydrocarbon Research Institute, Chemistry Department, University of Southern California, Los Angeles, California 90089-1661

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Introduction. Block copolymers are technologically important and have been the object of substantial scientific investigations.[1] Phase separation of blocks is frequently observed. Such systems may function as non-cross-linked composites where one phase reinforces the other. One of the most generally applicable methods to make block copolymers in which individual block length and composition are clearly defined is the anionic living polymerization of two or more monomers in a sequential manner as first described by Szwarc.[2,3] Such methods are useful for the preparation of thermoplastic elastomers from two incompatible polymer phases such as styrene and butadiene.[1,4] Anionic block copolymers are typically difficult to prepare from single-pot mixtures due to the dissimilarity of reactivity of many monomers to anion sources. Chain termination/transfer may also lead to a mixture of homopolymers. Nevertheless, a few examples of graded, or tapered, block copolymers have been reported.[5,6]

The anionic ring-opening (AROP) copolymerization of mixtures of 1,1-dimethyl-1-silacyclopent-3-ene (**I**) and 1-methyl-1-phenyl-1-silacyclopent-3-ene (**II**) is found to produce block copolymers of the type $A_x(AB)_yB_z$ where AB denotes a tapered region between the two homoblocks. The microstructure of the 6:4 copolymer is shown to be predominately a long block of 1,1-dimethyl-1-sila-*cis*-pent-3-ene (A) units, a shorter block of 1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene (B) units, and a tapered region between the two homoblocks which is rich in B. DSCs of the copolymers show two distinct T_gs resulting from domain separation of the two homoblocks. Electron microscopy of the milky-white 6:4 copolymer shows phase separation. These results are interpreted in terms of monomer reactivity.

Instrumental Section. Polymer microstructure was studied by ^1H and ^{13}C NMR by use of a Bruker AMX-500, 500-MHz FT-NMR. The spectra are referenced to chloroform. ^{29}Si spectra were obtained on a Bruker SY-270, 270-MHz FT-NMR and are referenced externally to TMS. High-resolution ^1H and ^{13}C spectra were obtained with digital resolution of 0.1 Hz/Pt. DSCs were obtained on a Perkin-Elmer DSC-7 fitted with a glovebox and purged with purified nitrogen. Electron micrographs (SEM) were obtained on a Cambridge stereoscope-360 instrument of solvent-cast thin films, sputter-coated with gold. GPC analysis was carried out on a Waters system, and molecular weights reported are referenced to monodisperse polystyrene standards.

Experimental Section. The copolymers were prepared by an AROP reaction which is similar to those used to prepare poly(1,1-disubstituted sila-*cis*-pent-3-enes).[7] To a 50-mL round-bottomed flask, containing a Teflon-covered magnetic stirbar, is distilled 20 mL of a dry THF solvent. The flask is fitted with a rubber septum and purged with UHP argon. HMPA (50 μL), 4.5 mmol of **I**, and 3.5 mmol of **II** are added via syringe.[7] The flask and its contents are cooled to −78 °C and allowed to equilibrate. *n*-Butyllithium (40 μL, 2.5 M; Aldrich) is added via syringe. The reaction is allowed to proceed for 3 h, at which time it is terminated with methanol. After workup,[7] the copolymer was precipitated twice from THF/methanol and dried on a high-vacuum line. The GPC of the copolymers has a broad monomodal peak, typical of poly(1-sila-*cis*-pent-3-enes) (Table I).

Table I. 6:4 Copolymer Results

monomer feed (%)		polym composn (%)[a]			
A	B	A	B	GPC M_w/M_n	T_g (°C)
56	44	51	49	226 100/107 700	−64/−20

[a] Determined by ^1H NMR integration.

Results and Discussion. As shown in Figures 1 and 2, the ^1H and ^{13}C NMR spectra of the 6:4 copolymer have microstructures dominated by the presence of two large blocks of A and B. The ^1H spectrum for this copolymer is surprisingly simple. The signals assigned to the methyl groups on silicon are sensitive to the polymer microstructure. The dimethylsilylene units give rise to three signals assigned on the basis of triad analysis. The intensities of these signals are not in a statistical distribution which would correspond to a random copolymer. Rather the siganl at 0.01 ppm, assigned to homoblock A_x, is most intense. It accounts for 64% of the dimethylsilylene signal areas. Similarly, the methylphenylsilylene units give rise to three signals for these methyl groups. These can be similarly assigned. The most intense resonance, at 0.25 ppm, may be assigned to the homoblock of B_z. This accounts for 44% of the methylphenylsilylene signal area. Thus, the average D_p of the A block is 630 and the average D_p of the B block is 280.

The ^{13}C NMR vinyl region at ca. 122–124 ppm can likewise be interpreted in terms of a diblock copolymer. Resonances at 123.10 and 123.25 ppm correspond to those found in the homopolymers of **I** and **II**, respectively.[8] In addition, signals are found in two clusters centered at 122.46 and 123.92 ppm. These may be assigned to the tapered region between the two blocks where random triads predominate. Furthermore, the *ipso* carbon signals of B show three clusters of signals. These signals are attributed to the pure B_z block and to the tapered region of an essentially random copolymer composed of B and A.

A total of four signals are detected in the ^{29}Si spectrum for this material. A broad resonance at −4.36 ppm corresponding to the average A_x block is seen. Three signals are observed at 2.23, 2.36, and 2.37 ppm. These resonances are due to the B_z block and tapering region.

Careful fractionation of the block copolymer allowed for the separation of the material into higher and lower molecular weight fractions. The lower weight material had a M_w value of 193 700 and was richer in B units (52%). The higher weight material had a M_w value of 270 200 and was considerably richer in A units (67%). No spectral differences other than peak areas in these fractions were observed. Neither homopolymer was isolated by this fractionation.

The DSC of the copolymers clearly shows the existence of two T_gs (Figure 3). The low T_g (−65 °C) corresponds well to that found for the homopolymer poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene).[7] The higher transition (−20 °C) is slightly lower than that found for the homopolymer poly(1-methyl-1-phenyl-sila-*cis*-pent-3-ene) (−16 °C).[7] The tapered region may act to lower the T_g for the B_z block

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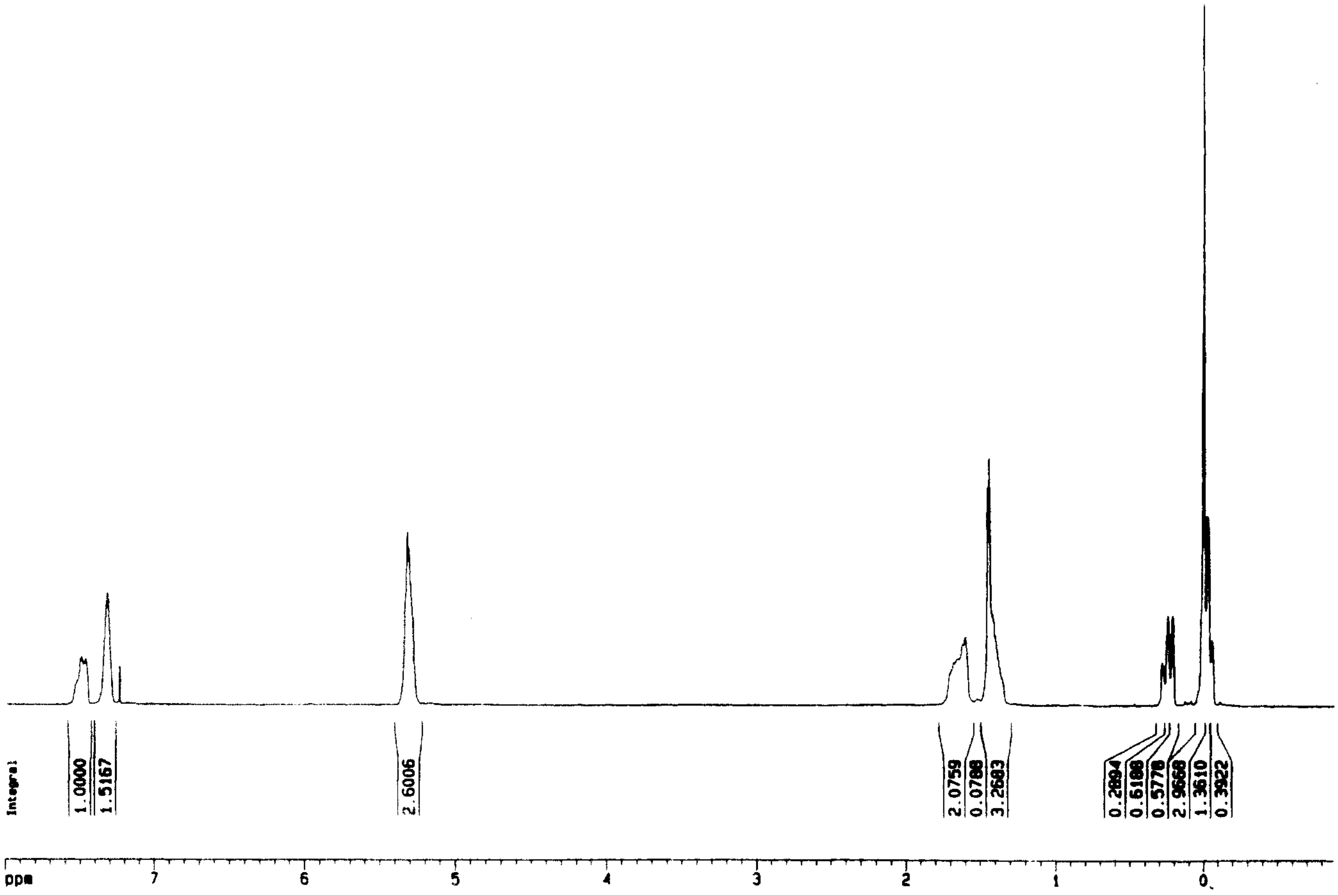

Figure 1. ^{1}H NMR spectroscopic data (500.1 MHz).

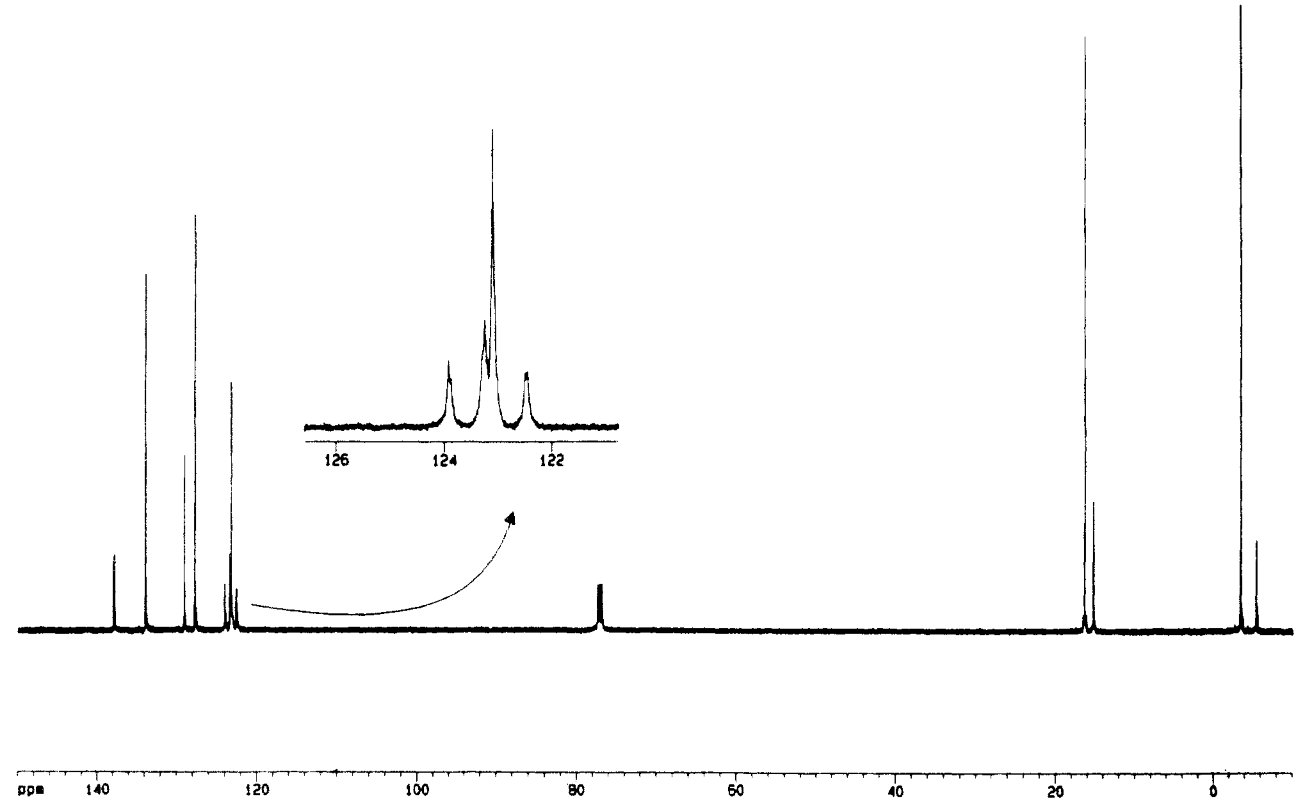

Figure 2. ^{13}C NMR spectroscopic data (126 MHz).

due to its relative shortness in relation to the A block, i.e., D_p 280 vs 630.

Electron microscopy of the copolymer shows the existence of nonuniform domains (Figure 4). These domains are highly diverse in size, although they are an average size of ~150 nm. The variation in size and the deformation within the sample may be due to the overall high polydispersity within this copolymer system. Conversely, these irregular domains may be due to the presence of incomplete block separation within the polymers through

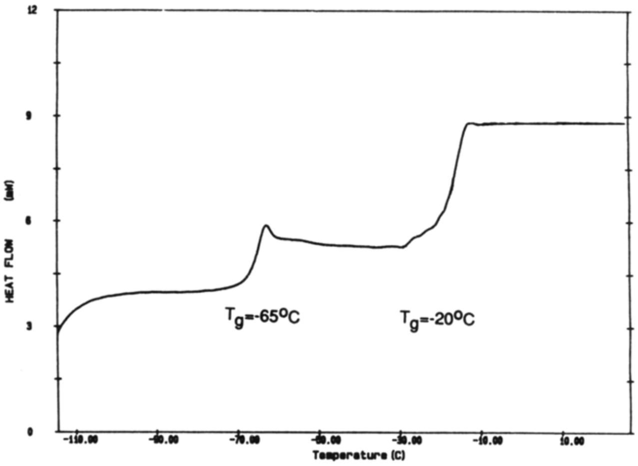

Figure 3. DSC curve for the 6:4 copolymer.

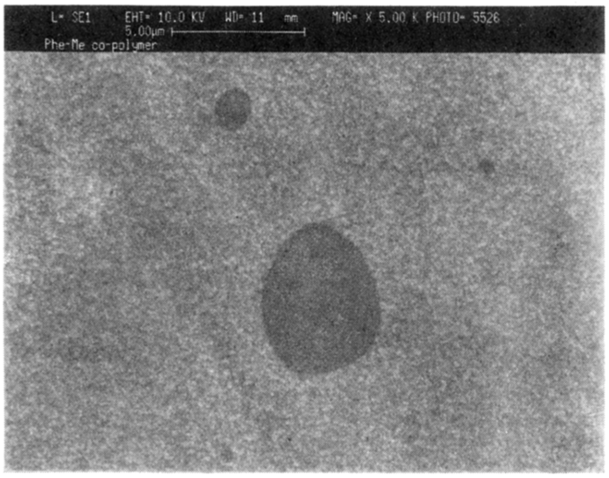

Figure 4. Electron micrograph of the 6:4 copolymer.

the tapering zone. TEM was not possible for our copolymer due to the similarity of chemical reactivities of each block; i.e., both are unsaturated allylic carbosilanes. TEM of block copolymers often relies on the specific reaction of one block.[8] For example, the polyisoprene block of a copoly(styrene/isoprene) has been stained for TEM by the reaction of the C–C double bonds with osmium tetroxide.[9]

Previously, the copolymerization of 1,1-dimethyl-1-silacyclopent-3-ene and 1,1-diphenyl-1-silacyclopent-3-ene (**III**) has been reported to produce low molecular weight materials ($<1 \times 10^4$). The microstructure of these was described as random.[10] The copolymers produced from **I** and **III** were of too low a molecular weight to show domain separation with the resultant effect that two T_gs were not observed. A single, average, T_g was observed for the copolymers of **I** and **III**. In the present case, the molecular weight of the material is sufficiently high to allow for domain separation, and apparently the entropy of mixing is low. The resultant effect is the observation of two T_gs and resolvable domains observed by electron microscopy.

Pentacoordinate siliconate species have been proposed to be essential intermediates in AROP.[11] The propagating intermediate formed from **I** is inductively destabilized by two methyl groups, whereas that from **III** is inductively stabilized by two phenyl groups. Resonance effects of aryl groups attached to silicon are small. Additionally, the steric bulk of the two phenyl groups in **III** would make attack of an allyl anion on **III** less favored. The overall stability of the siliconate intermediate from **II** is influenced by both factors. The more reactive siliconate intermediate formed from **I** leads to a higher molecular weight polymer. The higher molecular weight fraction of the copolymer was richer in A units, while the lower molecular weight fraction was richer in B units. These observations are consistent with a mechanism for AROP which is dependent upon the nature of the R groups on silicon.

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