

Bulk anionic ring opening polymerization of silacyclopent-3-enes

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Summary

Poly[1,1-diphenyl-1-sila-*cis*-pent-3-ene](I), poly[1,1-dimethyl-1-sila-*cis*-pent-3-ene](II), poly[1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene](III), poly[1-methyl-sila-*cis*-pent-3-ene](IV), and poly[1-phenyl-1-sila-*cis*-pent-3-ene](V) were prepared by bulk anionic ring opening polymerization of the corresponding 1-silacyclopent-3-enes, at room temperature by use *n*-butyllithium or *t*-butyllithium and HMPA as co-catalysts. No solvent (THF or diethyl ether) was utilized.

Introduction

Stereoregular poly[1-sila-*cis*-pent-3-enes] have previously been prepared by the anionic ring opening polymerization of the corresponding 1-silacyclopent-3-enes in THF (1-4) or diethyl ether (5) at low temperature (-40 to -78°C) by use of alkylolithium and HMPA, TMEDA or DMPU as co-catalysts. While these reactions proceed readily in high yield, experimentally they are difficult to carry out on preparative scale. Specifically, the ether solvents must be rigorously purified by distillation from sodium benzophenone ketyl under inert atmosphere immediately prior to use. The ever present possibility of the formation of hydroperoxide impurities in ether solvents is an additional concern. Maintenance of low reaction temperature requires specialized cooling equipment. In this paper, we report a simplified stereoregular high yield polymerization of 1-silacyclopent-3-enes to the corresponding poly[1-sila-*cis*-pent-3-enes].

Experimental

Monomers and reagents

Monomers were prepared by published procedures (1-5).

HMPA was redistilled and stored over activated molecular sieves (4Å) in a Mininert syringe valve container. *n*-Butyllithium, 2.5M in hexane, and *t*-butyllithium, 2.0M in hexanes, were purchased from Aldrich and were titrated before use (6).

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Spectral and physical characterization

^1H and ^{13}C NMR spectra were recorded using a Bruker AM-250 spectrometer operating in the Fourier transform mode. ^{13}C NMR spectra were obtained with broad band proton decoupling.

DSC was carried out with a Perkin-Elmer DCS-7 Instrument fitted with a complete glove box. The box was purged with purified nitrogen gas. The instrument was calibrated with hexane (mp -95°C) and water (mp 0°C). Liquid nitrogen was used as a cooling bath.

The molecular weight distribution of the polymers was determined GPC on a Waters system. This was comprised of a U6K injector, a 510 HPLC solvent delivery system, a R401 differential refractometer, and a Maxima 820 control system. A Waters 7.8mm x 30 cm Ultrastaygel linear column packed with $<10\mu\text{m}$ 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 against known polystyrene standards.

Bulk polymerization

A 25 mL round bottom flask, containing a Teflon covered stir bar, was fitted with a septum and purged under ultra high purity argon stream. Monomer (2.0g), and $50\mu\text{L}$ of HMPA were introduced via syringe and allowed to stir at room temperature for about ten minutes. *n*-Butyllithium or *t*-butyllithium, $100\mu\text{L}$, was added via syringe in one portion and the mixtures were stirred for three hours. During the course of the reaction the viscosity of the solution typically increased rapidly. In the case of **I**, the viscosity increased to the point that the mixture could no longer be stirred with a magnetic stirrer. The polymer solutions were a deep red color, except for **IV** and **V** which were a light yellow color, right to the point of termination with methanol.

The polymerizations were quenched via the addition of $200\mu\text{L}$ of methanol and the mixtures were pipetted into a centrifuge tube. Hot chloroform was added to dissolve the polymer completely. This took approximately one to three mLs. The polymers were then precipitated using methanol and centrifuged. Before analysis the polymers were completely dried on a high vacuum line.

Bulk polymerization leading to polymers **I** through **VII** were conducted in a similar manner. A reaction in which TMEDA was used in place of HMPA produced no polymer, and only starting material was recovered.

Results and discussion

Polymers **I-VII** were synthesized in good yields with modest to good molecular weights and polydispersities (Table I). ^1H and ^{13}C NMR are identical to those


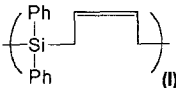

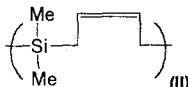

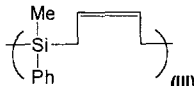



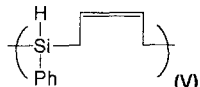



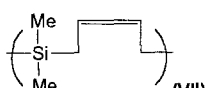
Monomer	Initiator	Polymer	GPC(M_w/M_n)	Yield
	<i>n</i> -butyllithium	 (I)	6000/4100	86%
	<i>n</i> -butyllithium	 (II)	13100/7160	81%
	<i>n</i> -butyllithium	 (III)	19300/11800	71%
	<i>n</i> -butyllithium	 (IV)	16900/2700	85%
	<i>n</i> -butyllithium	 (V)	2610/2050	63%
	<i>t</i> -butyllithium	 (VI)	11300/6710	91%
	<i>t</i> -butyllithium	 (VII)	52900/27500	89%

Table I; Polymers prepared.

previously reported for stereoregular *cis* polymers I-VII. In systems II & III, the molecular weights were clearly lower than those attainable from high dilution low temperature reactions in THF (1-4). In systems I & V molecular weights and polydispersities were similar to those seen for low temperature, ether solvent systems (1-3).

Interestingly, in the case of IV, the molecular weight of the polymer is approximately a factor of ten higher than that previously prepared (2). Although, the polydispersity

is also higher. Higher polydispersity may be due to the formation of crosslinks in the system via the displacement of hydride (Fig. 1). Such crosslink points are not seen in the NMR of this systems, however few of them would be needed to increase the polydispersity and therefore may not be observed. Similar branching has been reported for poly[1-sila-cis-pent-3-ene] (7). This may occur by nucleophilic displacement of hydride from a silyl center by a propagating allyl anion (8,9). Displacement of pendant alkyl or aryl groups from silicon has not been seen. An alternative explanation for high polydispersity would depend upon descriptions of monomer/initiator and monomer/polymer reactivity.

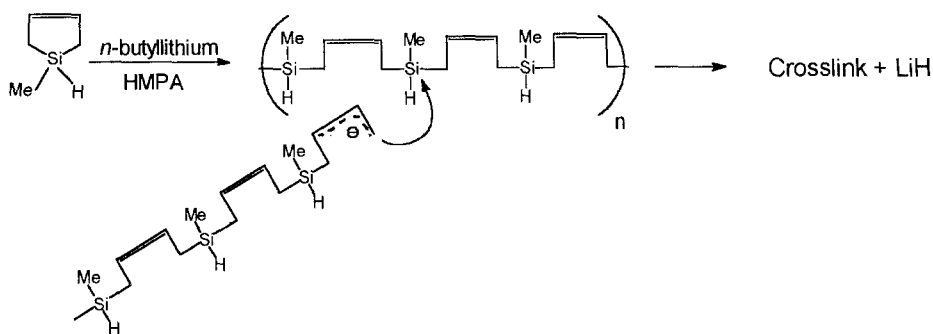


Figure 1; Potential crosslinking pathway in **V**.

Overall the molecular weights and yields of polymers **I-V** are similar. This may be due to viscosity effects within the polymerization systems. In the absence of solvent, the viscosity of the monomer/polymer solutions increases very rapidly. Mechanical stirring then becomes difficult. In the case of **I**, the solution becomes solid within 20 minutes. Living chains can no longer grow as they become less solvated, and diffusion of the monomer throughout the system becomes the controlling factor in the polymerization.

The role of HMPA in these systems is to coordinate the alkyllithium and increase its basicity (10,11). Additionally, the HMPA solubilizes the base into the organic medium. An experiment carried out with TMEDA rather than HMPA produced no polymer. HMPA provides an excellent means to activate the base and allow polymerization in a system where solubility is critical. TMEDA apparently is incapable of functioning in the absence of THF solvent. It has been established that TMEDA is often a less effective complexing agent than HMPA. Switching from *n*-butyllithium to *t*-butyllithium (**VI** and **VII**) increases both the molecular weight and overall yield of these polymers. It is well known that *t*-butyllithium is a more reactive alkyllithium reagent (11). It may be that aggregation of initiated polymer chain ends is a factor in the polymerization of *n*-butyllithium but is less important in the polymerization with *t*-butyllithium.

The bulk polymerization of 1-methyl-silacyclopent-3-ene can be used to produce a polymer of sufficient molecular weight for the measurement of T_g . Previously reported preparations of poly[1-methyl-sila-*cis*-pent-3-ene] (IV) produced low molecular weight material which did not lend themselves to accurate DSC measurements. The DSC curve for this polymer is given in figure 2. This data is in good agreement with that predicted for poly[1-methyl-1-substituted-sila-*cis*-pent-3-enes] comb like materials (12).

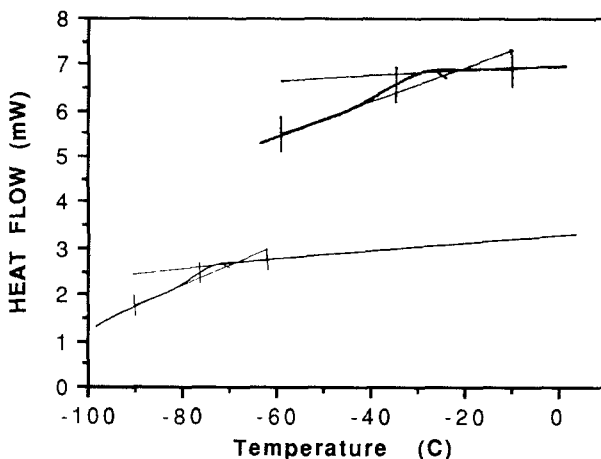


Figure 2; DSC of V.

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