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Partial and complete chemical modification of poly(1,1-dimethyl-1-sila-cis-pent-3-ene) by addition of dichloroketene

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Partial and complete chemical modification of poly(1,1-dimethyl-1-sila-cis-pent-3-ene) by addition of dichloroketene

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(Received 12 December 1990; accepted 8 March 1991)

Dichloroketene, generated by the ultrasound-promoted dechlorination of trichloroacetyl chloride with zinc, has been added to the carbon–carbon double bonds of poly(1,1-dimethyl-1-sila-cis-pent-3-ene) (poly-1). The molecular-weight distribution of the adduct polymer in which all of the carbon–carbon double bonds have reacted with dichloroketene, poly[2,2-dichloro-cis-3,4-bis(methylene)cyclobutanone dimethylsiline], 100% poly[1-C1C-C-O], has been characterized by gel permeation chromatography. The microstructure of 100% poly[1-(Cl2C=C=O)] has been elucidated by 1H, 13C and 29Si nuclear magnetic resonance as well as by infra-red spectroscopy. Similarly, a series of random copolymers have been prepared in which only some of the carbon–carbon double bonds of poly-1 have reacted with dichloroketene. These have been characterized as above. The glass transition temperatures (Tg) of these copolymers, as well as that of 100% poly[1-(Cl2C=C=O)], have been determined by differential scanning calorimetry. The Tg values are found to increase linearly with the percentage of the carbon–carbon double bonds of poly-1 that have reacted with dichloroketene.

(Keywords: dichloroketene; addition; Tg values; copolymers)

INTRODUCTION

Dichloroketene (II) is well known to undergo cycloaddition reactions with the C–C double bonds of alkenes1. These [2 + 2] cycloaddition reactions proceed stereospecifically via a concerted [π2 + π2] reaction in which the π-system of the alkene and the C–C double bond of the ketene approach each other via an orthogonal trajectory2. These reactions yield 2,2-dichloro-3,4-disubstituted cyclobutanones in which the geometrical relationship of the substituents is identical to that in the starting alkene. i.e. cis-alkenes yield cis-cyclobutanones and trans-alkenes yield trans-cyclobutanones.

Unlike less reactive ketenes, II reacts even at room temperature with the C–C double bonds of unactivated alkenes, such as cyclopentene and cyclohexene3. Even with 1,3-dienes, which might react with II via a [2 + 4] pathway, [2 + 2] cycloaddition products (2,2-dichlorocyclooctanones) are obtained4–6. For example, [2 + 2] cycloaddition reaction of II with one of the C–C double bonds of 5-trimethylsilylecyclopentadiene yields 7,7-dichloro-4-exo-trimethylsilylbicyclo[3.2.0]hept-2-en-6-one7,8. Despite considerable interest in the reactions of allylic silanes9, this is the only case of such a reaction. The facile generation of II under mild experimental conditions from inexpensive readily available starting materials recommends this reaction. II can be generated either by the homogeneous dehydrohalogenation of dichloroacetyl chloride with triethylamine or by the heterogeneous dechlorination of trichloroacetyl chloride with active zinc10. The recent observation that ultrasound promotes this heterogeneous reaction further facilitates the preparation of 2,2-dichlorocyclobutanones11.

2,2-Dichlorocyclobutanones are themselves versatile synthetic intermediates. For example, they can easily be converted to cyclobutanones by the dissolving metal reduction of the C–Cl bonds12. This transformation can also be achieved by reaction with tri-n-butyltin hydride13. They can likewise be modified under basic conditions to yield 2-alkoxycyclopropane carboxylic acids via a Favorskii-type ring contraction reaction14–15.

Despite the high reactivity of II discussed above, no examples of its reactions with C–C double bonds of unsaturated polymers such as cis-1,4-polybutadiene have been reported. This is surprising since there is considerable interest in the chemical modification of polymers16–19. Modification of functional groups in a polymer is one of the general routes for the synthesis of new polymeric materials. Many such reactions lead...
Addition of difluorocarbene to poly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene). Thermal stability and characterization of microstructures by $^1$H, $^{13}$C, $^{19}$F and $^{29}$Si NMR spectroscopy.

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Addition of difluorocarbene to poly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene). Thermal stability and characterization of microstructures by $^1$H, $^{13}$C, $^{19}$F and $^{29}$Si n.m.r. spectroscopy

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Excess difluorocarbene, generated by the sodium iodide catalysed decomposition of trifluoromethylphenylmercury, adds in a stereospecific cis manner to the carbon–carbon double bonds of poly[1-methyl-1-phenyl-1-sila-cis-pent-3-ene] (I) to yield poly[1,3,4-difluorocyclohexyl-1-methyl-1-phenyl-1-sila-cis-pent-3-ene] (F,C:C). Similarly, a series of random copolymers has been prepared in which only some of the carbon–carbon double bonds of I have reacted with difluorocarbene. The microstructures of these difluorocyclopropanated polymers have been determined by $^1$H, $^{13}$C, $^{19}$F and $^{29}$Si n.m.r. spectroscopy.

The glass transition temperatures of these copolymers are found to depend on the extent of difluorocyclopropanation. The thermal stability of F,C:C has been determined by thermogravimetric analysis. The thermal stability of I, F,C:C, poly[1,3,4-dichlorocyclohexyl-1-methyl-1-phenyl-1-sila-cis-pent-3-ene] (Cl,C:C) and (1-methyl-3,4-dimethylene-1-phenyl-1-sila-cis-pent-3-ene) (H,C:C) are compared.

(Keywords: difluorocarbene; copolymers; microstructure)

INTRODUCTION

There is considerable interest in the chemical modification of polymers$^{1-4}$. Such reactions permit the preparation of polymers which cannot be prepared by monomer polymerisation. In addition, partial chemical modification permits the synthesis of novel copolymers. Carbene addition to unsaturated polymers is one method for facile derivatisation. For example, dichloro- and difluorocarbene add stereospecifically to the carbon–carbon double bonds of cis- and trans-1,4-polybutadiene$^{5-9}$.

We have previously added dichlorocarbene to the carbon–carbon double bonds of I and found the polymer Cl,C:C to undergo facile chain scission at low temperature (95 C)$^{10}$. This degradation probably occurs by a two-step mechanism. The first involves ionization of one of the carbon–chlorine bonds with concerted disrotatory opening of the cyclopropane ring to yield an allylic cation. This symmetry-allowed process is accelerated due to stabilization of the allylic cation by the two adjacent methylphenylsilyle groups. It is well known that silicon has a profound stabilizing effect on $\beta$-carbocation centres$^{11}$. Subsequent nucleophilic attack by the chloride anion on an adjacent methylphenylsilyle centre results in scission of the polymer chain (equation 1). F,C:C is expected to be more stable than Cl,C:C if the first step in this process is rate determining since ionization of a carbon–fluorine bond will occur less readily than that of a carbon–chlorine bond$^{12}$. On the other hand, if nucleophilic attack on one of the methylphenylsilyle centres that is $\beta$ to the allylic carbocation is rate limiting, then we might anticipate that the difluorocarbene adduct polymer would decompose more rapidly since a silicon–fluorine bond is much stronger than a silicon–chlorine bond$^{13}$.

A series of copolymers composed of 1-methyl-1-phenyl-1-sila-cis-pent-3-ene(I) and 3,4-difluoromethyl-1-methyl-1-phenyl-1-sila-cis-pent-3-ene(III) units has been prepared by controlling the extent of the difluorocyclopropanation of the carbon–carbon double bonds of I, in the hope that these will have predictable physical properties between those of I and F,C:C.

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**Title and Subtitle**

Dimerization and polymerization of 2,3-benzo-5-silaspiro-[4.4]nona-2,7-diene.

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Dimerization and Polymerization of 2,3-Benzo-5-silaspiro[4.4]nona-2,7-diene

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ABSTRACT: Treatment of 2,3-benzo-5-silaspiro[4.4]nona-2,7-diene (I) with catalytic amounts of n-butyllithium and hexamethylphosphoramide (HMPA) in THF results in dimerization of I to give 2,3:12,13-dibenzo-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene (II). On the other hand, ring-opening metathesis polymerization (ROMP) of I cocatalyzed by tungsten hexachloride and tetraphenyltin gives poly[(3,4-benzo-1-silacyclopent-3-en-1-y1ene)-cis- and -trans-but-2-en-1,4-ylene] (cis- and trans-III).

Introduction

We have been interested in the ring-opening polymerization of 1-silacyclopent-3-ene. These reactions generally lead to poly[(1-sila-cis-pent-3-enes)]. Recently, we studied the anionic polymerization of several 5-silaspiro[4.4]nona-2,7-diene systems and found that dimerization competes with polymerization in some of these cases. In an attempt to better understand the factors controlling this competition, we studied both the anionic and ring-opening metathesis polymerization of 2,3-benzo-5-silaspiro[4.4]nona-2,7-diene (I).

Results and Discussion

2,3-Benzo-5-silaspiro[4.4]nona-2,7-diene (I) was prepared from benzyl(chloromethyl)dichlorosilane (IV) (Figure 1). This aluminum chloride catalyzed intramolecular Friedel-Crafts cyclization of IV gives 1,1-dichloro-3,4-benzo-1-silacyclopent-3-ene (V), which reacts with 1,3-butadiene and magnesium in THF to yield I.

Treatment of I with catalytic amounts of n-butyllithium and HMPA did not result in anionic ring-opening polymerization and formation of poly[(3,4-benzo-1-silacyclopent-3-en-1-y1ene)-cis-but-2-en-1,4-ylene] (cis-III) but rather in formation of a dimer 2,3:12,13-dibenzosiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene (II) (Figure 2). By comparison, both 1,1-dimethyl-1-silacyclopent-3-ene and 1,1-dimethyl-3,4-benzo-1-silacyclopentene undergo anionic ring-opening polymerization to yield respectively poly(1,1-dimethyl-1-sila-cis-pent-3-ene) and poly(1,1-dimethyl-3,4-benzo-1-silapentene).

The anionic dimerization of I to yield II may be related to the dimerization of 2,3-benzo-5-silaspiro[4.4]nona-2,7-diene (VI) which gives 2,3:12,13-tetramethyl-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene (VII), whose structure has been rigorously established by X-ray crystallography. The molecular weight of II was determined by mass spectrometry while its structure was established by 1H, 13C, and 29Si NMR as well as by IR and UV spectroscopy. In particular, the 29Si NMR resonance for I is found at 33.51 ppm while that for II is observed at 19.12 ppm, an upfield shift of 14.44 ppm. This is similar to the 13.7 ppm upfield shift that is observed when the 29Si NMR resonance for VI (25.54 ppm) is compared to that of VII (11.87 ppm). In addition, the chemical shifts of the vinyl protons and carbons are consistent with structure II. In particular, the vinyl protons of I are observed at 6.08 ppm while those for II are found at 5.39 ppm. By comparison, the 'H NMR signals for the vinyl protons of VI are found at 5.91 ppm while those of VII are observed at 5.30 ppm. Likewise, the allylic, benzylic and vinyl 13C NMR signals of I and II can be compared to those of VI and VII (Table I). The nature of the factors which favor dimerization of I and VI under anionic catalysis is not fully understood.

On the other hand, ring-opening metathesis polymerization of I cocatalyzed by tungsten hexachloride and tetraphenyltin with activation by cyclopentene is successful and results in cis- and trans-III (Figure 3). Ring-opening metathesis polymerization reactions are often stereospecific but not stereospecific. Tungsten hexachloride and tetraphenyltin have been frequently utilized as catalysts for ROMP. Cyclopentene has been previously utilized to activate such ROMP catalytic systems.

The stereochemical composition of III can be determined by integration of the allylic and vinyl hydrogen resonances. Specifically the 'H NMR signal at 1.94 ppm is assigned to the allylic hydrogens of trans-III units, while the resonance at 1.97 ppm is assigned to cis-III units. Likewise, the 1H NMR signal at 5.20 ppm is assigned to the vinyl hydrogens of trans-III units while that at 5.25 ppm results from the cis-III units. Integration of these is consistent with a polymer composed of 16% trans-III units and 84% cis-III units.

The 13C and 29Si NMR of the 3,4-benzo-1-silacyclopent-3-en-1-ylene (VIII) units are sensitive to microenvironment (Figure 4). Three 29Si NMR signals are observed. These can be accounted for on the basis that the but-2-en-1,4-ylene (IX) units on either side of VIII units can be both cis-IX, one cis-IX and one trans-IX, or both trans-IX. The microenvironment for VIII with cis-IX on either side is most probable while that with trans-IX units on either side is least probable. The 29Si NMR
Anionic dimerization and ring-opening polymerization of 1,1-divinyl-1-silacyclopent-3-ene


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Anionic Dimerization and Ring-Opening Polymerization of 1,1-Divinyl-1-silacyclopent-3-ene

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ABSTRACT: Anionic ring-opening polymerization of 1,1-divinyl-1-silacyclopent-3-ene (I) cocatalyzed by n-butyl lithium and hexamethylphosphoramide (HMPA) in THF at low temperature (−78 °C) leads to a mixture of 1,1,6,6-tetra vinyl-1,6-dialicycloclo deca-3,8-diene (dimer) and poly(1,1-divinyl-1-silacyclopent-3-ene) (polymer). These have been separated and characterized by 1H, 13C, and 29Si NMR, IR, and UV spectroscopy and elemental analysis. The molecular weight of the dimer has been determined by mass spectrometry, while the molecular weight distribution of the polymer has been measured by gel permeation chromatography (GPC). Thermogravimetric analysis (TGA) of the polymer in nitrogen gave a 62% char yield. The glass transition temperature (Tg) −65 °C of the polymer was determined by differential scanning calorimetry (DSC). The mechanism of this reaction has been studied.

Introduction

The proposal by Yajima that poly(1-methyl-1-sila-ethane) [CH3SiHCH3], is a key intermediate in the conversion of poly(dimethylsiloxane) into α silicon carbide has stimulated considerable interest in the chemistry of polycarbosilanes.1 Saturated polycarbosilanes such as poly(1,1-dimethyl-1-silbutane) and poly(1,1-dimethyl-1-silbeethane) have been prepared by anionic2-4 platinum-catalyzed,5 and thermal6,7 ring-opening polymerization of 1,1-dimethyl-1-silacyclobutane and 1,1,3,3-tetramethyl-1,3-disilacyclobutane, respectively. We have been interested in the preparation of sterically unsaturated polycarbosilane such as poly(1-sila-cis-pent-3-ene).10-12 These have been prepared by the anionic ring-opening polymerization of 1-silacyclopent-3-ene. Studies designed to elucidate the mechanism of these polymerization reactions have shown a number of unusual features. For example, 1,1,3,4-tetramethyl-1-silacyclopent-3-ene undergoes exchange of alkyl groups bonded to silicon rather than polymerization on treatment with n-butyl lithium and hexamethylphosphoramide (HMPA) in tetrahydrofuran (THF) at low temperature.11 This observation as well as the presence of 1-methyl-1-silacyclopent-3-ene end groups in poly(1,1-methyl-1-sila-cis-pent-3-ene)13,14 has been interpreted in terms of the importance of anionic hyper-valent siliconate intermediates in these polymerization reactions (see Figure 1).

In this paper, we report that anionic ring-opening polymerization of 1,1-divinyl-1-silacyclopent-3-ene yields poly(1,1-divinyl-1-silacyclopent-3-ene) (polymer) as expected. This carbosilane polymer has a very high degree of unsaturation and is converted on thermal decomposition to a high char yield. However, of greater mechanistic interest, significant amounts of 1,1,6,6-tetra vinyl-1,6-dialicycloclo deca-3,8-cyclodecadiene (dimer) are isolated along with the polymer. Experiments on the effect of monomer concentration and temperature on the ratio of dimer to polymer provide additional understanding of the mechanism of this reaction. The observation that pure polymer can be equilibrated to a mixture of dimer and polymer under polymerization reaction conditions is particularly significant (see Figure 2).

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ABSTRACT: Anionic ring-opening polymerization of 1,1-divinyl-1-silacyclopent-3-ene (I) cocatalyzed by n-butyl lithium and hexamethylphosphoramide (HMPA) in THF at low temperature (−78 °C) leads to a mixture of 1,1,6,6-tetra vinyl-1,6-dialicycloclo deca-3,8-diene (dimer) and poly(1,1-divinyl-1-silacyclopent-3-ene) (polymer). These have been separated and characterized by 1H, 13C, and 29Si NMR, IR, and UV spectroscopy and elemental analysis. The molecular weight of the dimer has been determined by mass spectrometry, while the molecular weight distribution of the polymer has been measured by gel permeation chromatography (GPC). Thermogravimetric analysis (TGA) of the polymer in nitrogen gave a 62% char yield. The glass transition temperature (Tg) −65 °C of the polymer was determined by differential scanning calorimetry (DSC). The mechanism of this reaction has been studied.

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**Title and Subtitle**

Stereoselective anionic ring opening polymerization of 1,1-dimethyl-1-silacyclobutene

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Stereoselective anionic ring opening polymerization of 1,1-dimethyl-1-silacyclobutene

Characterization of poly(1,1-dimethyl-1-sila-cis-but-2-ene)

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SUMMARY

Stereoselective anionic ring opening polymerization of 1,1-dimethyl-1-silacyclobutene co-catalyzed by n-butyllithium and hexamethyldiphosphoramide (HMPA) in THF at -78°C yields predominantly poly(1,1-dimethyl-1-sila-cis-but-2-ene). The polymer has been characterized by $^1$H, $^{13}$C, $^{29}$Si NMR spectroscopy, gel permeation chromatography (GPC), thermogravimetric analysis (TGA) and elemental analysis.

EXPERIMENTAL

$^1$H and $^{13}$C NMR spectra were obtained on a Bruker AM-360 spectrometer operating in the Fourier Transform mode (FT). $^{29}$Si NMR spectra were recorded on an IBM-Bruker WP-270-SY spectrometer. Five to ten percent weight/vol% solutions of polymer in chloroform-d were used for $^1$H NMR spectra, whereas fifteen percent solutions were utilized for $^{13}$C and $^{29}$Si NMR spectra. $^{13}$C NMR spectra were run with broad band proton decoupling. A heteronuclear gated decoupling pulse sequence (NOE) with a 20 sec delay was used to acquire $^{29}$Si NMR spectra (1). These were externally referenced to TMS. Chloroform was used as an internal reference for $^1$H and $^{13}$C NMR spectra. IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer.

Gel permeation chromatographic analysis of the molecular weight distribution of the polymer was performed on a Waters system comprised of a U6K injector, a 510 HPLC solvent delivery system, a 4001 refractive index detector and a Model 820 Maxima control system. A Waters 7.8 mm x 30 cm Ultrastyragel linear column packed with less than 10 m particles of mixed pore size crosslinked styrene divinylbenzene copolymer maintained at 20°C was used for the analysis. The eluting solvent was HPLC grade THF at a flow rate of 0.8 mL/min. The retention times were calibrated against those of known monodisperse polystyrene standards: $M_0$ = 612,000; 114,000; 47,500; 18,700 and 5,120 whose $M_w/M_n$ are less than 1.09.

Thermogravimetric analysis of the polymer was carried out on a Perkin-Elmer TGS-2 instrument with a nitrogen flow rate of 40 cm$^3$/min. The temperature program for the analysis was 5°C/min for 10 min followed by an increase of 4°C/min to 750°C.

Elemental analysis was performed by Galbraith Laboratories, Knoxville TN.

All reactions were carried out under an atmosphere of argon in flame dried glassware. THF was dried by distillation from a deep blue solution of sodium/benzophenone ketyl immediately prior to use. HMPA was distilled from calcium hydride and stored over activated 4 A$^3$ molecular sieves.

1,1-Dimethyl-1-silacyclobutene (I)

I was prepared by flash vacuum pyrolysis of diallyldimethylsilane (Aldrich) at 750°C. The $^1$H and

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Anionic Ring-Opening Polymerization of 2,3-Benz0-1-silacyclobutenes. Characterization of Poly(2,3-benzo-1-silabutenes)

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ABSTRACT: Anionic ring-opening polymerization of 2,3-benzo-1,1-dimethyl-1-silacyclobutene (I), 2,3-benzo-1-methyl-1-phenyl-1-silacyclobutene (II), and 2,3-benzo-1,1-diphenyl-1-silacyclobutene (III) catalyzed by n-butyllithium and hexamethylphosphoramide (HMPA) in THF at low temperature (-78 °C) yields respectively poly(2,3-benzo-1,1-dimethyl-1-silabutene) (IV), poly(2,3-benzo-1-methyl-1-phenyl-1-silabutene) (V), and poly(2,3-benzo-1,1-diphenyl-1-silabutene) (VI). These polymers have been characterized by 1H, 13C, and 29Si NMR as well as by IR and UV-visible spectroscopy. Their molecular compositions have been determined by elemental analysis. The molecular weight distributions of these polymers have been measured by gel-permeation chromatography (GPC), their thermal stabilities by thermogravimetric analysis (TGA), and their glass transition temperatures (Tg) by differential scanning calorimetry (DSC).

Introduction

While there has been considerable work done on the ring-opening polymerization of silacyclobutanes, the polymerization of 2,3-benzo-1-silacyclobutene systems has been less thoroughly studied. This paper reports the synthesis and characterization of poly(2,3-benzo-1,1-dimethyl-1-silacyclobutene) (IV), poly(2,3-benzo-1-methyl-1-phenyl-1-silacyclobutene) (V), and poly(2,3-benzo-1,1-diphenyl-1-silacyclobutene) (VI). These polymers were prepared by the anionic ring-opening polymerization of 2,3-benzo-1,1-dimethyl-1-silacyclobutane (I), 2,3-benzo-1-methyl-1-phenyl-1-silacyclobutene (II), and 2,3-benzo-1,1-diphenyl-1-silacyclobutene (III), respectively.

Experimental Section

1H, 13C, and 29Si NMR spectra were obtained on an IBM-Bruker 270-SY spectrometer operating in the Fourier transform mode. 13C NMR spectra were run with broad-band proton decoupling. Ten to fifteen percent solutions in chloroform-d were used to obtain 13C and 29Si NMR spectra. Five percent solutions were used to obtain 1H NMR spectra. Chloroform or TMS were utilized as an internal standard for 1H and 13C NMR spectra. A heteronuclear gated decoupling pulse sequence (NONOBE) with a delay of 20 s was used to obtain 29Si NMR spectra which were externally referenced to TMS. IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer of neat liquid samples on sodium chloride plates or as potassium bromide pellets for solids. UV spectra were recorded on a Shimadzu UV-260 UV-visible spectrometer. Spectra quality THF was used to prepare solutions of polymers, and spectral quality hexane was used to prepare solutions of monomers for UV spectrophotometry.

Gel permeation chromatographic (GPC) analysis of the molecular weight distribution and refractometric determination of molecular weight were performed on a Waters system. This was comprised of a U6K injector, a 510 A fraction collector, and a WISP sample station. A 7.8 mm × 30 cm Waters Ultrastra-gel linear column packed with 10 μm particles of mixed pore size, cross-linked styrene–divinylbenzene copolymer was used for the analysis. The eluant was HPLC-grade THF at a flow rate of 0.8 mL/min. Retention times were calibrated against known monodisperse polystyrene standards Mw/Mn = 179 000, 110 000, 20 400, and 1350 whose Mw/Mn are less than 1.09.

Preparative GLPC was carried out on a Waters system equipped with a 1/4 in. × 10 ft stainless steel column packed with 10% SE-30 on Chromosorb W and 20% on 80/100 mesh. The column was deactivated immediately prior to use by injection of 50 μL of hexamethyldisilazane.

Thermogravimetric analysis (TGA) of the polymer was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 cm3/min. The temperature program for these analyses was 50 °C for 10 min followed by an increase of 5 °C/min to 100 °C. After 10 min at 100 °C the temperature was increased at a rate of 5 °C/min to 750 °C. The glass transition temperature (Tg) and the melting point (Tm) were determined by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC-4 system. The initial temperature for the analysis was 30 °C. This was increased at a rate of 20 °C/min to 200 °C. The melting points of the polymers were also measured on an Electrothermal melting point apparatus and are uncorrected.

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.

Tetrahydrofuran (THF) was distilled immediately prior to use from sodium benzophenone ketyl. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride and was stored over 4 Å molecular sieves. Hexane was distilled from lithium aluminum hydride. n-Butyllithium in hexane (2.5 M) and 2-bromobenzyl bromide (Aldrich) were used as received. Dime-thyldichlorosilane, methylphenylidichlorosilane, and diphenyl-dichlorosilane were obtained from Hela. They were purified by fractional distillation.

All glassware was dried overnight in an oven at 120 °C and was flame dried prior to use. All reactions were conducted under an atmosphere of purified argon.

2,3-Benz0-1,1-dimethyl-1-silacyclobutene (I). 1 I was prepared by the reaction of 2-bromobenzyl bromide and dimethylchlorosilane with magnesium powder in THF. The product was purified by fractional distillation through a 15-cm vacuum-jacketed Vigreux column. A fraction (bp 106/107 °C/60 mm (lit.7 73 °C/17 mm) of 17 g (44% yield) was isolated. 1H NMR δ 0.36 (s, 6 H), 2.06 (s, 2 H), 7.03 (m, 2 H), 7.15 (s, 2 H), 13C NMR: δ -0.45, 20.13, 126.18, 126.91, 130.38, 130.46, 145.94, 150.55. 29Si NMR: δ 8.41. IR: δ 3056, 2960, 2909, 1586, 1450, 1436, 1282, 1297, 1043, 849, 833, 768, 718 cm-1. UV: λmax nm (ε) 219 (5300), 283 (1200), 269 (1700), 276 (1550).

2,3-Benz0-1-methyl-1-phenyl-1-silacyclobutene (II). In a 500-mL three-necked round-bottom flask equipped with a reflux condenser, a pressure equalizing addition funnel, and a Teflon-covered magnetic stirring bar was placed magnesium powder (9.7 g, 0.4 mol) and ether (30 mL). A mixture of 2-bromobenzyl bromide (33 g, 0.13 mol) and methylphenylidichlorosilane (26.8 g, 0.4 mol) in ether (150 mL) was placed in the addition funnel.
Synthesis and characterization of poly(l-methyl-1-silabutane), poly(l-phenyl-1-silabutane) and poly(1-silabutane)

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Synthesis and characterization of poly(1-methyl-1-silabutane), poly(1-phenyl-1-silabutane) and poly(1-silabutane)

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Summary:

Anionic ring opening polymerization of 1-methyl-1-silacyclobutane, 1-phenyl-1-silacyclobutane and 1-silacyclobutane co-catalyzed by n-butyllithium and hexamethylphosphoramide (HMPA) in THF at -78°C yields poly(1-methyl-1-silabutane), poly(1-phenyl-1-silabutane) and poly(1-silabutane) respectively. These saturated carbosilane polymers possess reactive Si-H bonds. They have been characterized by 'H, '13C and '29Si NMR as well as FT-IR and UV spectroscopy. Their molecular weight distributions have been determined by gel permeation chromatography (GPC), thermal stabilities by thermogravimetric analysis (TGA) and glass transition temperatures (T_g) by differential scanning calorimetry (DSC).

Introduction

While polymethylhydrosiloxanes are well known commercial products (1), polycarbosilanes which possess reactive Si-H bonds have only recently attracted significant attention. The proposal by Yajima that poly(1-methyl-1-silaethane) (-CH2-SiH-CH2-)n is an intermediate in the pyrolytic conversion of poly(dimethylsilane) fibers into silicon carbide fibers (2,3) stimulated interest in such systems (4,5). Oligo(1-silapropane) has been prepared by hydrosilation polymerization of vinyldichlorosilane to yield poly(1,1-dichloro-1-silapropane) followed by reduction of the Si-Cl bonds with lithium aluminum hydride (6,7). Low molecular weight poly(1-methyl-1-sila-cis-pent-3-ene) and poly(1-sila-cis-pent-3-ene), carbosilane polymers which contain both reactive Si-H and carbon-carbon double bonds have been prepared by anionic ring opening polymerization of 1-methyl-1-silacyclopent-3-ene and 1-silacyclopent-3-ene respectively (8,9).

\[
\text{Si-H} \xrightarrow{\text{n-BuLi/HMPA}} \text{THF/-78°C} \xrightarrow{\text{H}} \text{Si-H}_n
\]

Experimental

'H and '13C NMR spectra were obtained on a Bruker AM-360 spectrometer operating in the Fourier Transform mode (FT). '29Si NMR spectra were recorded on an IBM-Bruker WP-270-SY spectrometer. Five to ten percent weight/volume solutions of polymer in chloroform-d were used for 'H NMR spectra, whereas fifteen to twenty percent solutions were utilized for '13C and '29Si NMR spectra. '13C NMR spectra were run with broad band proton decoupling. A heteronuclear gated decoupling pulse sequence (NONOE) with a 20 sec delay was used to acquire '29Si NMR spectra (10).

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Synthesis of carbosilane monomers and polymers with mesogenic pendant groups

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Introduction

Liquid crystalline (LC) materials demonstrate unusual phase behavior which combine properties of the homogeneous liquid and the ordered crystalline states. Polymeric side chain LC materials comprised of a flexible, low T_g siloxane backbone in which the silyl centers are substituted with pendant mesogens have been prepared. The low T_g (-64°C) of poly(1,1-dimethyl-1-sila-cyclopent-3-ene) suggests that materials based on stereoregular unsaturated carbosilane backbones, substituted with pendant arylxy groups, might exhibit LC behavior at rt. Such materials would represent a novel class of liquid crystalline substances.

Experimental

1HF was distilled from a dark blue solution of sodium benzophenone ketyl under nitrogen. HMPA was distilled over calcium hydride and stored over sieves (4Å) in a syringe sealed container. Chloroplatinic acid (Aldrich) was used without further purification. n-Butyllithium (Aldrich) was titrated before use. Allyl phenyl ether (Aldrich) was redistilled before use. 4-Allyloxybiphenyl, 2-allyloxynaphthalene, 1-methyl-1-sila-cyclopent-3-ene, 1-phenyl-1-sila-cyclopent-3-ene were prepared by literature procedures.

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

Monomer synthesis

Monomers were prepared by H_2PtCl_6 catalyzed hydrosilation reactions of 1-methyl-1-sila-cyclopent-3-ene or 1-phenyl-1-sila-cyclopent-3-ene and the corresponding allyl aryl ethers, as below.

1-Methyl-1-(3'-p-biphenoxypropyl)-1-sila-cyclopent-3-ene (II).

Polymer synthesis by Anionic Ring Opening Polymerization (AROP)

Monomers and polymers prepared for this study.

Table I. Monomers and polymers prepared for this study.

Characterization

The structures of the monomers and polymers were confirmed by ^1H, ^13C and ^29Si NMR spectroscopy. The molecular weight distribution of the polymers was determined by GPC on a Waters system. TGA was carried out on a Perkin-Elmer TGS-2 instrument. The thermal transitions of the polymers were determined by DSC on a Perkin-Elmer DSC-7.

Polarizing optical microscopy (POM) was done using a Unitron polarizing microscope fitted with a Leitz/Omega hot stage. The polymer films were heated to 80°C and then cooled at 0.5°C/min. Micrographs were obtained at various temperatures at a magnification of 100x with a Polaroid camera attachment.
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Synthesis and Properties of Novel Functionally Substituted Carbosilane Polymers

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Abstract: Polv(3'-cyanopropyl)-1-methyl-1-silabutane, poly(1-methyl-1-[3'-(glycidyloxy)propyl]-1-silabutane, poly(1-methyl-1-[4',7',10'-tetracosatetradecanyl]-1-silabutane, poly(1-methyl-1-[3'-(phenyloxy)propyl]-1-silabutane, and poly(1-methyl-1-[3'-(perfluorophenyl)propyl]-1-silabutane have been prepared by the platinum-catalyzed hydrocarbon graft reactions between poly(1-methyl-1-silabutane) and the appropriate functional alkene. These polymers have been characterized by 1H, 13C, 19F (where appropriate), and 29Si NMR as well as by FT-IR and UV spectroscopy. The molecular weight distributions of these polymers have been determined by gel permeation chromatography (GPC), their thermal stabilities by thermogravimetric analysis (TGA), and their glass transition temperatures by differential scanning calorimetry.

While there has been considerable work over the last 50 years on silicone polymers, there has been much less work on carbosilane polymers. The observation of Yajima that thermal decomposition of poly(methylsilylene) [CH2SiHCH2]n results in loss of methane and hydrogen and formation of β-silicon carbide has stimulated considerable interest in poly(carbosilanes). Closely related to these polymeric systems have a siloxane backbone in which some or all of the silyl centers carry functional (dimethylsilicones) such as low surface tension, high thermal stability, and low glass transition temperature with properties which are associated with the pendant functional chain. For example, poly[methyl-(3,3,3-trifluoropropyl)]siloxane combines thermal stability and low glass transition temperature with lubricating properties and lack of swelling in hydrocarbon solvents characteristic of perfluoroalkyl polymers. Poly(1-(3'-cyanopropyl)-1-methylsiloxane) compounds find utility as thermally stable polar liquid phases for gas–liquid chromatography, while similar chemically bonded siloxane polymers are used in high-pressure liquid chromatography. Poly(3'-aminopropyl)methylsiloxane, poly(3'-acryloxy)propyl)methylsiloxane, poly(3'-mercaptopropyl)methylsiloxane, poly(3'-cyanopropyl)methylsiloxane, and poly(3'-glycidyloxy)propyl)methylsiloxane are among the silicone polymers with pendant functionally substituted alkyl groups which are commercially available.

Closely related to these are siloxane graft copolymers. These polymeric systems have a siloxane backbone in which some or all of the silyl centers carry functional substituted oligomeric side chains. Important examples of this type of polymer are polysiloxanes substituted with hydrophilic nonionic oligo(oxethylens) pendant groups. These find commercial application as surfactants and are of scientific interest due to their ability to complex lithium cations to form solvent-free polymer electrolytes which have reasonable ionic conductivities. These have been prepared by the platinum-catalyzed hydrosilation.
Synthesis, characterization and platinum catalyzed cross-linking of copoly(1-silacyclobut-1-ylidene-1,4-phenylene).

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SYNTHESIS, CHARACTERIZATION and PLATINUM CATALYZED CROSSLINKING OF COPOLY(1-SILACYCLOBUT-1-YLIDENE-1,4-PHENYLENE). PROPERTIES OF AROMATIC CARBOSILANE THERMOSET

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ABSTRACT:

Low molecular weight copoly(1-silacyclobut-1-ylidene-1,4-phenylene) has been prepared by the reaction of 1,1-dichloro-1-silacyclobutane with di-Grignard reagent prepared from dibromobenzene. The resulting polymer was characterized by 'H, 13C and 29Si NMR as well as FT-IR and UV spectroscopy. Molecular weight distribution has been determined by GPC and its thermal stability by TGA in both nitrogen and air. Thermal degradation of 1,1-nitrogen gives high (60-82%) char yield. Tg of 1 has been measured by DSC. Platinum catalyzed opening of the strained silacyclobutane rings crosslinks 1. The resulting polymer, when cast on a Perkin-Elmer TGS-2 instrument, exhibits a high Tg and low dielectric constant indicating that this material is potentially useful as a dielectric constant and dissipation factor are reported.

Introduction:

1,1,3,3-Tetraphenylsilacyclobutane underwent platinum catalyzed 1,2 thermal polymerization to give a high molecular weight polymer which upon casting on a glass plate at 170°C and allowing the solvent to evaporate, showed a high Tg and low dielectric constant. The resulting polymer was characterized by FT-IR and UV spectroscopy and the results are reported in this paper.

Experimental:

'HD and 13C NMR spectra were run on a Bruker AM-250 spectrometer operating in the FT mode. 29Si NMR spectra were recorded on a Bruker 200 ST spectrometer. 13C NMR spectra were run with broad band proton decoupling. 29Si NMR spectra were obtained by use of a heteronuclear gated decoupling pulse sequence (INVETAG) with a pulse delay of 15 20 x 15 13C and 29Si NMR spectra were obtained in 15% solution of chloroform-d. 1H NMR spectra were obtained in 5% solution of chloroform-d. DMSO-d6 spectra were recorded on an IBM FT-IR-30S spectrometer at a flow rate of 0.7 mL/min. The retention times were determined by GPC using a Shimadzu UV-200 spectrometer.

The molecular weight distribution of this polymer was determined by GPC on a Waters system comprised of a U6K injector, a 510 HPLC solvent delivery system, a 41 differential refractometer and a Maxima 820 control system. Waters 7.8 mm x 30 cm ultrasyrny column packed with 10 μm particles of mixed pore size crosslinked styrene-divinylbenzene copolymer was utilized for the analysis. The column was maintained at 70°C. 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 47,500, 18,700, 5,120 and 2,200 whose Mw, Mn values are 1 09.

TG was carried out on a Perkin-Elmer TGS-2 instrument with a nitrogen flow rate of 40 cm/min. The temperature program for the analysis was 50°C for 2 min. The temperature was then increased at a rate of 5°C/min to 750°C. Tg of 1 was determined by DSC on a Perkin-Elmer DSC-7 instrument. The melting point of indium (156°C) and spectral grade n-hexane (-95°C) were utilized to calibrate the DSC. The temperature scans were begun at 100°C for 5 min. The temperature was then increased at a rate of 20°C/min to 150°C. DMTA of cured materials was performed on a Polymer Laboratories DMTA Mk II. A standard single cantilever bending head (-150-300°C) was used. The analysis was carried out at frequencies of 0.1, 1 and 5 Hz at a strain level of 2%. The temperature was increased at 40°C/min. Dielectric constant and dissipation factor were determined on a DuPont DEA-2970 Dielectric Analyzer.

The thermal stability of Pt cured 1,1,3,3-tetraphenylsilacyclobutane was determined by TGA in nitrogen. The major difference between the Pt cured and non-cured sample is that the initial weight loss is eliminated. The initial weight loss is probably due to low molecular weight oligomers. Weight loss at high temperature (1000°C) is similar for both cured and Pt cured samples. This suggests that the degree of crosslinking of achieved by thermal and Pt crosslinking is similar.

The thermal stability of Pt cured 1,1,3,3-tetraphenylsilacyclobutane was determined by TGA in nitrogen. The major difference between the Pt cured and non-cured sample is that the initial weight loss is eliminated. The initial weight loss is probably due to low molecular weight oligomers. Weight loss at high temperature (1000°C) is similar for both cured and Pt cured samples. This suggests that the degree of crosslinking of achieved by thermal and Pt crosslinking is similar.

Copoly(1-silacyclobut-1-ylidene-1,4-phenylene) in a 500 mL three necked flask equipped with a rubber septum and a condenser, a pressure equalizing addition funnel and a Teflon covered magnetic stirring bar was placed in a nitrogen atmosphere. Nitrogen was bubbled through the solution for 10 min at 1 atm pressure. The reaction mixture was stirred at room temperature until the mixture had discolored (10-20 min) in THF (200 mL) was slowly added to the reaction mixture. After completion of the addition, the mixture was stirred for 30 min at the water 30 mL was added. The organic layer was separated and the aqueous layer was washed with 30 mL ether. The combined organic layers were dried over anhydrous magnesium sulfate and the volatile solvents were removed by evaporation under reduced pressure. The residue was dissolved in a minimum amount of THF and the polymer was precipitated with ethyl alcohol. The process was repeated twice. The polymer was dried under vacuum at 70°C. The sample was dried at 40°C for 10°C in vacuum at 10°C. The sample was then dried at 150°C in vacuum drying oven for 1 h and then at 200°C for another 1 h. Other samples of 1 were cured at 150°C for 3 h and then at 200°C for 5 h.

Results and Discussion:

I has been prepared by the reaction of the di-Grignard reagent prepared from 1,4-dibromobenzene with 1,1-dichloro-1-silacyclobutane. The resulting polymer was characterized by FT-IR and UV spectroscopy and the results are reported in this paper.

The thermal stability of I was determined by TGA in nitrogen. It is stable to 60°C. Between 60 and 250°C, it shows the least weight loss. Further weight loss occurs between 250°C and 400°C. Above 400°C, the weight loss is rapid. By 600°C, the weight loss is about 10% of the original weight of the sample. This high char yield probably results from thermal crosslinking due to opening of the silacyclobutane rings of 1 3.4

Figure 1. TGA of polymer in nitrogen.

The thermal stability of Pt cured I was also determined by TGA in nitrogen. The major difference between the Pt cured and non-cured sample is that the initial weight loss is eliminated. This initial weight loss is probably due to low molecular weight oligomers. Weight loss at high temperature (700°C) is similar for both cured and Pt cured samples. This suggests that the degree of crosslinking achieved by thermal and Pt crosslinking may be similar.

The thermal stability of Pt cured 1 was also measured in air. It was thermally stable to 250°C. Between 250 and 360°C, a 35% weight loss is observed. Between 365 and 500°C, an additional 15% weight loss is detected. Above 500°C, a second rapid weight loss occurs. No further weight loss is detected above 600°C (Figure 2).
Anionic polymerizations of trimethylvinylsilane and phenyltrimethylvinylsilane towards the synthesis of well-defined polyfluorodimethylvinylsilane & polyvinylalcohol.


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**ANIONIC POLYMERIZATIONS OF TRIMETHYLVINYLSILANE AND PHENYLDIMETHYLVINYLSILANE TOWARDS THE SYNTHESIS OF WELL-DEFINED POLYFLUORODIMETHYLVINYLSILANE AND POLYVINYLALCOHOL**

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**Introduction**

Over the last decade, polytrimethylvinylsilane (PTMVS) and polyphenylidimethylvinylsilane (PPDMVS) and their copolymers and polymer blends have been widely applied and studied as materials for gas-separation membranes (1-3), optical fibers (4), contact lenses (5,6), waterproofing fabrics (7), optical disks (8), semiconductor devices (9), etc. However, reactions of PTMVS and PPDMVS to give other potentially useful polymers have not been explored. Thus, narrow molecular weight distribution (MWD) PTMVS and PPDMVS might be useful as intermediates in the synthesis of monodisperse polyethylene, polyvinylalcohol, polyacrylene, polyvinylhalide, polynitroethylene and polynvinylamine (Scheme 1). Such polymers can not readily be synthesized.

**Scheme 1**

Anionic Polymerization of Trimethylvinylsilane (TMVS) and Phenylidimethylvinylsilane (PDMVS)

Silicon stabilizes a-carbanions due to its vacant d orbitals (10). Vinylsilanes such as TMVS and PDMVS are therefore good candidates for living anionic polymerizations. Anionic polymerization of TMVS and PDMVS was first reported by N. S. Nametkin et al. in 1965 (11). They synthesized oligomers (12), homopolymers (11), block- (13) and graft- copolymers (14) under various conditions (11,13,15,16). They also reported the occurrence of termination reactions resulting from hydride elimination (17,18). Later studies by Rickle confirmed such side reactions and their effects on MWD and yield (19,20). He also found that such side reactions were enhanced by the addition of ethers (20). We now wish to report the synthesis of monodisperse polyvinylsilanes by anionic polymerization and their attempted transformation into other polymers.

Synthesis of monodisperse polyfluorodimethylvinylsilane (PFDMVS) and polyvinylalcohol (PVA)

Protodesilylation and oxidation of various of organosilicon compounds had been recently demonstrated by Tamao (21,22,23), Fleming (24,25) and Nishiyama (26), but none of these involved polymers. We now wish to report on such transformations for PFDMVS employing similar reaction conditions (Scheme 2).

**Scheme 2**

(PDMS America Inc.) to a phenylmagnesium bromide/THF solution at -20°C followed by reflux for 2 hours. Over 70% isolated yield of product was obtained. Both TMVS and PDMVS were distilled from CaH2 twice under vacuum prior to use. Toluene was purified by stirring over fresh K-Na alloy under vacuum overnight. Tetrachlorofluoroboric acid-diethyl ether complex (85%) was purchased from Aldrich Chemical Co. PFDMVS was purified by reprecipitation in THF using MeOH as the non-solvent.

Polymerizations: Anionic polymerization was carried out by initiation of purified TMVS and PDMVS with n-, sec-, or tert-butyllithium in toluene at various temperatures (in the -70°C to 20°C range especially at the lower temperatures). The reaction usually took 12 hours to several days. The colorless solution was finally reacted with methanol and precipitated in cold MeOH. Polystyrene-b-TMVS block copolymers were synthesized via the same procedure.

Protodesilylation Reactions: The reaction of PFDMVS with HBF4.Et2O was carried out in a polypropylene vessel. Low MW of PFDMVS (DP=46) were first tried in order to obtain more complete substitution. The purified PFDMVS was dissolved in chloroform, and HBF4.Et2O was then introduced under argon. The reaction mixture was stirred at 60°C for 3 hours. During this protodesilylation process, the reaction temperature was carefully monitored in order to prevent boiling of the solvent and swelling of the plastic vessel. After evaporation of the volatile materials, the resulting fluorosilane polymer was characterized by 1H and 19F NMR and by SEC.

Oxidation Reactions: The PFDMVS obtained was dissolved in THF and transferred to a glass flask. A 15% KOH solution in MeOH was introduced into the reaction vessel followed by the dropwise addition of 30% H2O2 aqueous solution. The reaction mixture was refluxed (50°C) for 4-19 hours. The resulting polymer was not water-soluble indicating that conversion was incomplete. We then tried to use dioxane instead of THF/MeOH solvents following the same reaction procedure. We also tried replacing H2O2 by three equivalents of m-chloroperbenzoic acid (MCPBA) with an excess of triethylamine in THF/MeOH and refluxing for 19 hours.

**Results and Discussion**

In the synthesis of PTMVS and polystyrene-b-TMVS, best results were obtained at -20°C in toluene for four days. In the case of PDMVS, we carried out polymerization reaction in toluene at 0°C for 2 days and then raised temperature to 20°C for another 3 days, which always gave the best results. The MW of the polymers we obtained ranged from 3,000 to 23,000 with MWD's around 1.1 and yields of 90-95%. The long reaction...
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Bulk anionic ring opening polymerization of silacyclopent-3-enes

Steven J. Sargeant, Mark A. Tapsak, and William P. Weber*

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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 of 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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