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

Howard Shih Jen Lee and William P. Weber^a

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Dichioroketene, 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 dimethylsilylene]. 100% poly(1-Cl₂C==C=O), has been characterized by gel permeation chromatogiaphy. 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-I have reacted with dichloroketene. These have been characterized as above. The glass transition temperatures (T_g) of these copolymers, as well as that of 100% poly(1-Cl₂C==C==O), have been determined by differential scanning calorimetry. The T_g values are found to increase linearly with the percentage of the carbon-carbon double bonds of poly-I have reacted with dichloroketene.

(Keywords: dichloroketene; addition; Tz 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 $[\pi_s^2 + \pi_a^2]$ 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.



Trans-cyclooctene

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-dichloro-

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3-vinylcyclobutanones) are obtained⁴⁻⁶. For example, [2+2] cycloaddition reaction of II with one of the C-C double bonds of 5-trimethylsilylcyclopentadiene yields 7,7-dichloro-4-exo-trimethylsilylbicyclo[3.2.0]hept-2-en-6-one^{7.8}. 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 dichloroaceiyl 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 hydride¹². They can likewise be modified under basic conditions to yield x-alkoxycyclopropane carboxylic acids via a Favorskii-type ring contraction reaction¹³⁻¹⁵.

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

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

Howard Shih-Jen Lee and William P. Weber*

K. B. and D. P. Loker Hydrocarbon Research Institute, Department of Chemistry. University of Southern California, Los Angeles, California 90089-1661, USA (Received 15 March 1991, accepted 24 June 1991)

Excess difluorocarbene, generated by the sodium iodide catalysed decomposition of (trifluoromethyl iphenylmercury, adds in a stereospecific *cis* manner to the carbon carbon double bonds of poly(1-methyl-1phenyl-1-sila-*cis*-pent-3-ene) (1) to yield poly(3,4-difluoromethylene-1-methyl-1-phenyl-1-sila-*cis*-pent-3ene) (F_2C -1). 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 ¹H, ¹³C, ¹⁹F and ²⁹Si 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_3C -I has been determined by thermogravimetric analysis. The thermal stability of 1, F_2C -1, poly(3,4-dichloromethylene-1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) (Cl_2C -I) and (1-methyl-3,4-methylene-1-phenyl-1-sila-*cis*-pent-3-ene) (H_2C -I) are compared

(Keywords: difluorocarbene; copolymers; microstructure)

INTRODUCTION

There is considerable interest in the chemical modification of polymers¹⁻⁴. Such reactions permit the preparation of polymers which cannot be prepared by monomer polymerization. In addition, partial chemical modification permits the synthesis of novel copolymers. Carbene addition to unsaturated polymers is one method for facile derivatization. For example, dichloro- and difluorocarbene add stereospecifically to the carbon-carbon double bonds of *cis*- and *trans*-1,4-polybutadiene⁵⁻⁹.

We have previously added dichlorocarbene to the carbon-carbon double bonds of I and found the polymer Cl₂C-I to undergo facile chain scission at low temperature $(95 \text{ C})^{10}$. This degradation process 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 methylphenylsilyl groups. It is well known that silicon has a profound stabilizing effect on β -carbocation centres¹¹. Subsequent nucleophilic attack by the chloride anion on an adjacent methylphenylsilyl centre results in seission of the polymer chain (equation (1)), F₂C-I is expected to be more stable than Cl₂C-I 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 bond¹². On the other hand, if nucleophilic attack on one of the methylphenylsilyl centres that is β to the allylic carbocation is rate limiting, then we might anticipate that the diffuorocarbene adduct polymer would decompose *more* rapidly since a silicon-fluorine bond is much stronger than a silicon-chlorine bond¹³.



A series of copolymers composed of 1-methyl-1phenyl-1-sila-cis-pent-3-ene(II) and 3.4-difluoromethylene-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_2C -1.

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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-ylene)-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-enes. These reactions generally lead to poly(1-sila-cis-pent-3-enes).¹ 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.^{2,3} 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). Thus aluminum chloride catalyzed intramolecular Friedel-Crafts cyclization of IV gives 1,1-dichloro-3,4benzo-1-silacyclopent-3-ene (V),⁴ which reacts with 1,3butadiene 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-ylene)-cis-but-2-en-1,4-ylene] (cis-III) but rather in formation of a dimer 2,3:12,13-dibenzo-5,10disiladispiro[4.4.4.4]octadecn-2,7,12,14-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)¹ and poly(1,1-dimethyl-3,4-benzo-1-silapentene).⁵

The anionic dimerization of I to yield II may be related to the dimerization of 2,3-dimethyl-5-silaspiro[4.4]nona-2,7-diene (VI) which gives 2,3:12,13-tetramethyl-5,10disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene (VII), whose structure has been rigorously established by X-ray crystallography.³ 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 14.4 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 ¹H NMR signals for the vinyl protons of VI are found at 5.91 ppm while those of VII are



Figure 1. Synthesis of 2,3-benzo-5-silaspiro[4.4]nona-2,7-diene (I).



Figure 2. Treatment of I with n-butyllithium. Synthesis of 2,3: 12,13-dibenzo-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene (II).

observed at 5.30 ppm. Likewise, the allyl, benzyl 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 stereoselective but not stereospecific.⁶ Tungsten hexachloride and tetraphenyltin have been frequently utilized as catalysts for ROMP. Cyclopentene has been previously utilized to activate such ROMP catalyst systems.⁷

The stereochemical composition of III can be determined by integration of the allyl and vinyl hydrogen resonances. Specifically the ¹H 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-1silacyclopent-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

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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 :1) cocatalyzed by n-butyllithium and hexamethylphosphoramide (HMPA) in THF at low temperature (-78 °C) leads to a mixture of 1,1,6,6-tetravinyl-1,6-disilacyclodeca-3,8-diene (dimer) and poly(1,1-divinyl-1-sila-cis-pent-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 spectroscopy, 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 (T_{ij}) -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-silaethane) $[CH_3SiHCH_2]_n$ is a key intermediate in the conversion of poly(dimethylsilane) into β silicon carbide has stimulated considerable interest in the chemistry of polycarbosilanes.¹ Saturated polycarbosilanes such as poly(1,1-dimethyl-1-silabutane) and poly(1,1-dimethyl-1silasthane) have been prepared by anionic.2-4 platinumcatalyzed,⁵ and thermal⁶⁻⁹ 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 stereoregular unsaturated polycarbosilane such as poly(1-sila-cis-pent-3-enes).10-12 These have been prepared by the anionic ring-opening polymerization of 1-silacyclopent-3-enes. 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-butyllithium 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-methyl-1-sila-cis-pent-3-ene)13.14 has been interpreted in terms of the importance of anionic hypervalent 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-tetravinyl-1,6-disila-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).







Figure 2. Anionic dimerization-ring-opening polymerization of I.





Experimental Section

¹H, ¹²C, and ²²Si NMR spectra were recorded on a Bruker AM-360 spectrometer operating in the Fourier transform mode. ²³Si NMR spectra were obtained by use of heteronuclear gated decoupling pulse sequence (NONOE) with a pulse delay of 20 s.¹⁵ Five percent weight/volume solutions in chloroform-d were used to measure ¹H and ¹²C NMR spectra, whereas 15% solutions were utilized to obtain ²²Si NMR spectra.

The ratio of dimer to polymer was determined by integration of quantitative ¹³C NMR spectra. ¹³C T_1 values for dimer and polymer were determined using the inversion recovery method¹⁶ (Figure 3). Samples of polymer and of mixtures of dimer and polymer dissolved in chloroform-*d* were placed in 5-mm NMR tubes. These solutions were degassed by bubbling UHP argon through them for 2 h. The NMR tubes were then sealed. The spectra were obtained at 30 °C on a Bruker SY-270 FT spectrometer using a τ pulse of 12.4 μ s and a $\pi/2$ pulse of 6.2 μ s. Fifty-six scans were accumulated with relaxation delays of 0.01, 0.1, 0.5, 1.0, 5.0, 10.0, 20.0, 40.0, 80.0, and 120.0 seconds. Analysis of these data gives the ¹³C T_1 values for both the dimer and the polymer.

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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-dimeihyl-1-silacyclobutene co-catalyzed by *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF at -78^oC yields predominantly poly(1,1-dimethyl-1-sila-c/s-but-2-ene). The polymer has been characterized by ¹H, ¹³C, ²⁹Si NMR spectroscopy, gel permeation chromatography (GPC), thermogravimetric analysis (TGA) and elemental analysis.



EXPERIMENTAL

¹H 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/vn⁻¹: ne solutions of polymer in chloroform-*d* were used for ¹H NMR spectra, whereas fifteen 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 (1). These were externally referenced to TMS. Chloroform was used as an internal reference for ¹H and ¹³ 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 R401 refractive index detector and a Model 820 Maxima control system. A Waters 7.8 mm x 30 cm Uitrastyragel 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_p 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 cm³/min. The temperature program for the analysis was 50°C 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^D molecular sleves.

1,1-Dimethyl-1-silacyclobutene (i)

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

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Anionic Ring-Opening Polymerization of 2,3-Benzo-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 a-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) (V). These polymers have been characterized by ³H. 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 (T_{e}) 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-silabutene) (IV), poly(2,3-benzo-1-methyl-1phenyl-1-silabutene) (V), and poly(2,3-benzo-1,1-diphenyl-1-silabutene) (VI). These polymers were prepared by the 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-sillacyclobutene (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 ¹⁴ H NMR spectra. Chloroform or TMS were utilized as an internal standard for ¹⁴ H and ¹³C NMR spectra. A heteronuclear gated decoupling pulse sequence (NONOE) with a delay of 20 s was used to obtain ²⁹Si NMR spectra which were externally referenced to TMS.¹

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 spectraquality hexane was used to prepare solutions of monomers for UV spectroscopy.

Gel permeation chromatographic (GPC) analysis of the molecular weight distribution of the polymers was performed on a Waters system. This was comprised of a U6K injector, a 510 solvent delivery system, a R401 differential refractometer, and a Maxima 820 data station. A $7.8 \text{ mm} \times 30 \text{ cm}$ Waters Ultrastyragel 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 M_p 179 000, 110 000, 20 400, and 1350 whose M_w/M_a are less than 1.09.

Preparative GLPC was carried out on a Gow Mac 550 GC equipped with a 1/4 in. $\times 10$ ft stainless steel column packed with 10% SE-30 on Chromosorb W NAW 60/80 mesh. The column was descrivated immediately prior to use by injection of 50 μ L of hexamethyldisilazane.

Thermogravimetric analysis (TGA) of the polymers was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 cm³/min. The temperature program for these enalyses 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 (T_s) and the melting point (T_m) 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 2bromobenzyl bromide (Aldrich) were used as received. Dimethyldichlorosilane, methylphenyldichlorosilane, and diphenyldichlorosilane were obtained from Hüls. 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-Benzo-1,1-dimethyl-1-silacyclobutene (I).² I was prepared by the reaction of 2-bromobenzyl bromide and dimethyldichlorosilane with magnesium powder in ether following literature procedures. The product was purified by fractional distillation through a 15-cm vacuum-jacketed Vigreux column. A fraction [bp 106/10? °C/60 mm (lit.² 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), 7.18 (m, 2 H). ¹³C NMR: δ =0.45, 20.13, 126.18, 126.91, 130.38, 130.46, 145.94, 150.55. ²⁹Si NMR: δ 9.41. IR: ν 3056, 2960, 2909, 1586, 1450, 1436, 1282, 1247, 1043, 849, 823, 786, 718 cm⁻¹. UV: λ_{max} nm (ϵ) 219 (5300), 262 (1200), 269 (1700), 276 (1550).

2,3-Benzo-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 methylphenyldichlorosilane (26.8 g, 0.4 mol) in ether (150 mL) was placed in the addition funnel

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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-1silacyclobutane and 1-silacyclobutane co-catalyzed by *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF at -78°C yields poly(1-methyl-1-silabutane), poly(1phenyl-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) (-CH₃-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-CI 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).



Experimental

¹H 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 ¹H 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

Steven J. Sargeant and William P. Weber*

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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.¹² Polymeric, side chain³⁴, LC materials comprised of a flexible, low T_g siloxane backbone in which the silyl centers are substituted with pendant mesogens have been prepared.⁹ The low T_g (-64°C)⁶ of poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) suggests that materials based on stereoregular unsaturated carbosilane backbones, substituted with pendant aryloxy groups, might exhibit LC behavior at rt. Such materials would represent a novel class of liquid crystalline substances.



THF 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.⁷ Allyl phenyl ether (Aldrich) was redistilled before use. 4-Allyloxybiphenyl⁹, 2-allyloxynapthalene⁹,1-methyl-1-silacyclopent-3-ene¹¹ 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 H₂PtCl₈ catalyzed hydrosilation reactions of 1-methyl-1-silacyclopent-3-ene or 1-phenyl-1-silacyclopent-3-ene and the corresponding allyl aryl ethers, as below.

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

A flask, fitted with a rubber septum, is charged with 4-allyloxybiphenyl and 1-methyl-1-silacyclopent-3-ene. H₂PtCl₈, 1x10⁻³ Pt to allyl aryl ether, is added by syringe. The reaction is quenched after 4h via the addition of water/methanol. The organic layer was removed and the aqueous phase was extracted with ether. The combined organic layers were dried over CaCl₂. The product was purified by flash chromatography on a silica gel column using pentane/chloroform (1:1) as eluant. This removed the Pt complexes. A water white liquid was obtained in 70% yield. Table I, illustrates the monomers which have been prepared.

Polymer Synthesis by Anionic Ring Opening Polymerization (AROP)

Polymers were synthesized by AROP of the corresponding monomers using *n*-butyllithium and HMPA as co-catalyst in THF solvent, as below.

Poly-[1-methyl-1-(3'-phenoxypropyl)-1-sila-cis-pent-3-ene)(V).

A flask, containing a Teflon covered magnetic stirring bar, was fitted with a rubber septum. THF (10 mL), 100 μ L of HMPA and 0.50g of (II) were added by syringe. The flask was cooled to -78°C for 15 min, and *n*-butyllithium (120 μ E) was added via syringe to the stirred solution. The reaction was allowed to proceed for 3h and was quenched via the addition of sat. aq. NH₄CI. The organic phase was removed and the aqueous phase was extracted with ether (3x50mE). The combined organic phases were washed with water, dried over anhydrous CaCl₂, then filtered through a plug of glass wool The solvents were removed under reduced pressure to yield an opaque, gummy solid. The polymer was twice taken up in a minimum amount of THF, precipitated out of solution with methanol and then centrifuged. Finally, the polymer was dried under vacuum to give 0.43g (80% yield). Table I lists the polymers which were prepared.



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 an 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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ARSTRACT: Polv[1-(3'-cyanopropyl)-1-methyl-1-silabutane], poly[1-methyl-1-[3'-(glycidyloxy)propyl]-1silabutane], poly[1-methyl-1-[3'-(triethoxysilyl)propyl]-1-silabutane], poly[1-methyl-1-(4',7',10'-trioxaundecanyl)-1-silabutane], poly[1-methyl-1-(4',7',10',13'-tetraoxatetradecanyl)-1-silabutane], poly[1-methyl-1-[3'-(phenyloxy)propyl]-1-silabutane], and poly[1-methyl-1-[3'-(pentafluorophenyl)propyl]-1-silabutane] have been prepared by the platinum-catalyzed hydrosilation graft reactions between poly(1-methyl-1-zilabutane) and the appropriate functional alkene. These polymers have been characterized by ¹H, ¹²C, ¹³F (where appropriate), and ²³Si 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 (T_g 's) by differential scanning calorimetry.

While there has been considerable work over the last 50 years on silicone polymers,^{1,2} there has been much less work on carbosilane polymers. The observation of Yajima that thermal decomposition of poly(methylsilylenemethylene) [CH₃SiHCH₂]_n results in loss of methane and hydrogen and formation of β -silicon carbide^{3,4} has stimulated considerable interest in polycarbosilanes.⁵

This paper reports the preparation of saturated carbosilane polymers which have functionally substituted pendant alkyl chains. These have been prepared by the chemical modification, by platinum-catalyzed hydrosilation graft reactions between functional alkenes and the reactive Si-H bonds, of the saturated carbosilane polymer, poly(1-methyl-1-silabutane).⁶ There is considerable interest in the chemical modification of intact polymers since this method often permits the synthesis of polymers which cannot be prepared directly.^{7,8}



Background

Numerous types of silicone polymers with functionally substituted pendant alkyl chains have been prepared. The synthesis, chemical properties, and significant applications of these have been reviewed.⁹⁻¹² Some of these have

(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)siloxanel combines thermal stability and low glass transition temperature with lubricating properties and lack of swelling in hydrocarbon solvents characteristic of perfluoroalkyl polymers.13.14 Poly[1-(3'-cyanopropyl)-1-methylailoxane] compounds find utility as thermally stable polar liquid phases for gas-liquid chromatography, while similar chemically bonded silozane polymers are used in high-pressure liquid chromatography.13 Poly(3'aminopropyl)methylsilozane, poly[3'-(acryloxy)propyl]methylsilozane, poly(3'-mercaptopropyi)methylsilozane, poly(3'-cyanopropyl)methylsiloxane, poly[3'-(glycidyloxy)propyl]methylsilozane are among the silicone polymers with pendant functionally substituted alkyl groups which are commercially available.¹¹

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(oxysthylene) pendant groups. These find commercial application as surfactants¹⁶ and are of scientific interest due to their ability to complex lithium cations to form solvent-free polymer electrolytes which have reasonable ionic conductivities.¹⁷⁻³⁰ These have been prepared by the platinum-catalyzed hydrosi-

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

Charles X. Liao, Min Wei Chen and William P. Weber* D. P. and K. B. Loker Hydrocarbon Research Institute, Dept. of Chem., U. of Southern California, Los Angeles, CA 90089-1661

ABSTRACT:

Low molecular weight copoly(1:s)(acyclobut-1:y)(dene-1:4:pheny)(ene): 1) has been prepared by the reaction of 1:1:d)(chloro-1:s)(acyclobutane.(II) with the di-Grignard reagent prepared from p-d)(formodenzene. I has been characterized by 1H, 13C and 29S) NMR as well as FT-IR and UV spectroscopy is molecular weight distribution has been determined by GPC, and its thermai stability by TGA in both nitrogen and air. Thermai degradation of 1 in nitrogen gives high (60-62%) char yield. Tg of 1 has been measured by DSC. Platinum catalyzed ring opening of the strained silacyclobutane rings crosslinks I. The bending modulus log E1 tan δ and Tg of this thermoset material has been determined by OMTA. Electrical properties; d)(electric constant and d)(s)(patient).

Introduction:

1.1-Disubstituted-1-silacyclobutanes undergo platinum catalyzed 1.2 thermal 3.4 as well as anionic ring opening polymerization 5.8 Ring opening of silacyclobutane and 1.3-disilacyclobutane units has been utilized to crosslink polysilacyclobutasilazanes 9-12 Crosslinking is a essential requirement for the high yield conversion of organometallic polymers to ceramic materials 13.14 Silacyclobutanes have not been previously used to crosslink polycarbosilanes Condensation polymerization of aromatic di-Grignard reagent prepared from p-dibromobenzene with II leads to low molecular weight 1. This viscuous liquid has a low Tg. Platinum catalyzed crosslinking of 1 yields a thermoset material which has a Tg. above 170°C, high bending modulus, low dielectric constant and dissipation factor.



Experimental:

1H and 13C NMR spectra were run on a Bruker AM-250 spectrometer operating in the FT mode. 29Si NMR spectra was recorded on a Bruker 270-ST spectrometer 13C NMR spectra were run with broad oarid proton decoupling 29Si NMR spectra were obtained by use of a heteronuclear gated decoupling pulse sequence (INVGATE) with a pulse delay of 15-20 s 15-13C and 29Si NMR spectra were obtained in 15% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 15% solution of chloroform a 1H NMR spectra were obtained in 15% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution of chloroform a 1H NMR spectra were obtained in 5% solution spectra were obtained a spectra were obtained were provided on a 1H NMR spectra were obtained in 5% solution spectra were provided on a 1H NMR spectra were obtained were provided on a 1H NMR spectra were p

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 R401 differential refractometer and a Maxima 820 control system. A Waters 7.8 mm x 30 cm. Ultrastyragel linear column packed with < 10 μ m particles of mixed pore size crosslinked stryene-divinylbenzene copolymer was utilized for the analysis. The column was maintained at nt. The eluting solvent was HPLC grade THF at a flow rate 0.7 mLmin. The retention times were calibrated against known monodisperse polystyrene standards. 47,500, 18,700, 5,120 and 2,200 whose M_W-M_n values are < 1.09

TGA was carried out on a Perkin-Elmer TGS-2 instrument with a nitrogen flow rate of 40 cc/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 or 800°C. Tg of I was determined by OSC on a Perkin-Elmer DSC-7 instrument The metting 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 frequency of 0.1, 1 and 5 Hz at a strain level of 2. The temperature was increased at 4°C/min. Dielectric constant and dissipation factor were determined on a DuPont DEA-2970 Dielectric Analyzer.

THF was distilled from a deep blue solution of sodium/benzophenone ketyl prior to use. All reactions were conducted in dried glassware under argon Magnesium powder, 1.4-dibromobenzene and 1.3-divinyi-tetramethyldistloxane platinum complex (2-3% Pt) in xylene (Pt complex) (Huls) were used 1.1-Dichloro-1-silacyclobutane (II) was prepared by Grignard cyclization of 3-chloropropytrichlorosiane with magnesium powder in ethyl ether 16-18

Copoly(1-silacyclobul-1-ylidene-1,4-phenylene) (I)

In a 500 mL three necked to flask, equipped with a rubber septum, an efficient reflux condenser, a pressure equalizing addition furner and a Tetron covered magnetic stirring bar was placed magnesium powder 3.0, g, 124 mmol) and 1.4-di-bromobenzene (13.4, g, 56.8 mmol) in THE 200 mL. The reaction mixture was stirred at it until the magnesium had disacbeared (1.6.0, g, 56.7 mmol) in THE (200 mL) the reaction mixture was stirred at it until the magnesium had disacbeared (1.6.0, g, 56.7 mmol) in THE (20 mL) was slowly added to the reaction mixture was the disacbeared of the addition the mixture was stured for 4 h at reflux Water, 20 mL) was added. The organic layer was bedrated and added using each was bedrated and added using each was magnesium suitate. Hered on the residue was disact were removed anyonous magnesium suitate. Hered on the residue was discover anyonous of the polymer mas dried under vacuum in this way. 7, 5, 9, 90, % yield of the polymer mas dried under vacuum in this way. 7, 5, 9, 90, % yield of the polymer $T_0 = 2800$ M, Min = 2650 Mag. Mag. 237, 71 m, 441, 130 NMR & 1,43, 13,24, 133,76, 133,86, 134,45, 135,56, 136,03, 295, NMR & 6.72, 6.96, 7, 20, IR v, 3363, 3049, 2969, 2926, 2871, 1557, 1468, 1440, 1422, 1403, 1325, 1360, 1232, 1172, 1129, 1061, 1016, 961, 905, 881, 832, 784, 719, 690, 630 cm⁻¹, UV kmax, nm (ϵ), 240,2, 1,600, 266,2, 696,

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In a 100 minb flask, I (6.0 g) and Pt complex (150 uL) were dissolved to THE 20 mL). The solvent was removed under reduce pressure at a temperature \leq 70°C. The sample was dried at 40°C for 12 h under vacuum in a mold, it was cured at 150°C in vacuum drying oven for 1 h, and then at 200°C for another tin (A-i) Other samples of I were cured at 150°C for 3 h, and then at 200°C for 5 h (B-i). Results and Discussion

I has been prepared by the reaction of the di-Grinard reagent prepared from 1,4-dibromobenzene with it in THF. End groups phenyl p-bromophenyl, or silanol are important due to the www.molecular.weights of $12M_W/M_0 = 2.600/1,400$). These leads to extra signals in the 13C NMR spectra of 1, Bands at 3363, 1120 and 1128 cm⁻¹ assigned to SICH groups have been detected in the FT-IR spectra of 1.

The thermally stability of I was determined by TGA in choose I is stable to 60°C. Between 60 and 250°C, a 9% weight loss was observed. Little further weight loss occurs between 250 and 460°C. Above 460°C rapid weight loss occurs. By 620°C, 31% percent of the original weight of the sample whas been lost. No further weight loss was detected on heating to 800°C. A 60% char yield was obtained (Figure 1). This high char yield probably results from thermal crosslinking due to opening of the silacyclobutane rings of t 3.4.



Figure 1. TGA of polymer I 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 of I 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 (>200 °C) is similar for both cured and Pt cured samples. This suggests that the degree of crosslinking of achieved by thermal and Pt crosslinking may be similar.

The thermal stability of a Pt cured I was also measured in the air. It was thermally stable to 250°C. Between 250 and 365°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 620°C (Figure 2).

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ANIONIC POLYMERIZATIONS OF TRIMETHYLVINYL-SILANE AND PHENYLDIMETHYLVINYLSILANE TOWARDS THE SYNTHESIS OF WELL-DEFINED POLYFLUORO-DIMETHYLVINYLSILANE AND POLYVINYLALCOHOL Yaodong Gan, William P Weber, Surya Prakash, George A. Olah and Thieo E. Hogen-Esch Loker Hydrocarbon Institute Department of Chemistry University of Southern California Los Angeles, CA 90089

Introduction

Over the last decade, polytrimethylvinylsilane (PTMVS) and polyphenyldimethylvinylsilane (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, polyacetylene, polyvinylhalide, polynitroethylene and polyvinylamine (Scheme 1). Such polymers can not readily be synthesized.



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

Silicon stabilizes α -carbanions due to its vacant d orbitals (10). Vinvisilanes 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 We now wish to report the synthesis of ethers (20). 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 PPDMVS employing similar reaction conditions (Scheme 2)

Experimental

Materials: TMVS was purchased from Huls America Inc. PDMVS was synthesized by adding vinyldimethylchlorosilane



Scheme 2

(Huls 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. Tetrafluoroboric acid-diethyl ether complex (85%) was purchased from Aldrich Chemical Co PPDMVS 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 tertbutyllithium 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 PPDMVS with HBF4:Et2O was carried out in a polypropylene vessel. Low MW of PPDMVS (DP=46) were first tried in order to obtain more complete substitution. The purified PPDMVS 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 $^{\circ}$ C in toluene for four days. In the case of PDMVS, we carried out polymerization reaction in toluene at 0 $^{\circ}$ C for 2 days and then raised temperature to 20 $^{\circ}$ 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

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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 alkyllithium and HMPA, TMEDA or DMPU as co-catalysts. While these reactions proceed readily in high vield, 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 (4A) 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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