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Synthesis and characterization of a silarylene–siloxane–diacetylene polymer and its conversion to a thermosetting plastic

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Abstract

The synthesis and characterization of a linear silarylene–siloxane–diacetylene polymer **1** and its conversion to a highly cross-linked thermoset **4** are discussed. The linear polymer was prepared via polycondensation of 1,4-bis(dimethylaminodimethylsilyl)butadiyne, $[(CH_3)_2N–Si(CH_3)_2–C{\equiv}C–C{\equiv}C–(CH_3)_2SiN(CH_3)_2]$, **2** with 1,4-bis(hydroxydimethylsilyl)benzene **3**. Conversion to a thermoset **4** occurs through the diacetylene groups above 300 °C. The thermoset was observed to exhibit long-term thermo-oxidative stability up to 350 °C in air as determined by thermogravimetric analysis.

Keywords: Siloxane; Thermoset; High temperature

1. Introduction

The increasing need for high-temperature resistant materials has led to a vast amount of research into the area of inorganic–organic hybrid polymers. The combination of inorganic and organic functionalities into a single component has the potential of producing materials with unique properties, such as good processability and high thermo-oxidative stability. The high thermal stability can be attributed to the generally higher bond dissociation energy of inorganic functional groups. For example, the bond dissociation energy of the Si–O unit is 443.7 kJ/mol whereas the analogous C–O bond is 357.9 kJ/mol [1]. Accordingly, research into the synthesis and evaluation of functionalized poly(organosiloxanes) has become increasingly widespread for high temperature usage.

The preparation of silarylene–siloxane linear polymers began to receive intense interest when it was discovered that inclusion of the silarylene unit into the polysiloxane backbone resulted in an increased resistance to degradative side reactions at elevated temperatures [2]. Presumably, inclusion of a rigid aromatic unit makes formation of major degradation products such as six and eight membered cyclic siloxy compounds, which are thermodynamically more stable at elevated temperatures, much more difficult [3]. The unique combination of high-temperature stability and low-temperature flexibility have prompted the syntheses of many different examples of these polymers containing a myriad of functional groups [2]. Several reports have appeared on the preparation of such polymers containing vulcanizable vinylic side groups [4–6]. The thermal stability of the vinyl containing silarylene–siloxane polymers was clearly higher than those of the corresponding non-vinyl polymers [6]. This result was attributed to formation of cross-linked materials at elevated temperatures that reduced the production of volatile degradation products.

Silarylene–siloxane polymers are prepared by a step-growth reaction involving a nucleophilic substitution reaction. The most useful methods employed for the synthesis of silarylene–siloxane polymers involve the condensation of 1,4-bis(dimethylhydroxysilyl)benzene **3** with an active silane compound such as chlorosilanes [7], acetoxysilanes [8], and bis(amino)silanes [9]. All the leaving groups yield a byproduct that causes chain cleavage producing low molecular weight polymers. The occurrence of degradative side reactions between acidic or basic byproducts and the growing polymer chain has been shown to limit molecular weights and disrupt the truly alternating nature of the polymer structures [10]. The ureidosilane route has been reported to be the method of choice for producing high-molecular weight linear silarylene–siloxane polymers with exactly alternating structures [11]. The byproduct of this reaction is urea, which is a neutral species and does not participate in the chain cleavage process. However, the high sensitivity of the bis(ureido)silanes to nucleophiles

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including water requires the use of extremely dry solvents and gases and pure monomer for the polymerization reaction.

We have a long-standing interest in the preparation and evaluation of materials for high temperature applications. Recently, we have found that inclusion of diacetylene units into the main chain of carborane–siloxane [12–15], siloxane [16], and ferrocenyl-carborane–siloxane [17] polymers affords materials with excellent thermal and oxidative stabilities. The stability has been attributed to formation of a cross-linked or networked structure via the diacetylene units at elevated temperature. Herein, we report the synthesis of a novel silarylene–siloxane–diacetylene linear polymer **1** and its thermal conversion to a highly cross-linked plastic **4**. We have found the aminosilane-deficient method to be the practical choice for the preparation of silarylene–siloxane polymers containing diacetylene units in the main chain.

2. Experimental

2.1. Procedures and materials

Unless otherwise noted all syntheses were performed under an atmosphere of dry argon employing standard Schlenk techniques. *n*-Butyllithium was purchased from Aldrich Chemical Co. and titrated before use [18]. Hexachlorobutadiene was purchased from Aldrich Chemical Co. and distilled before use at 86–89 °C and 8 Torr. Dimethylaminodimethylchlorosilane was purchased from Gelest Inc. and distilled before use. 1,4-Bis(hydroxydimethylsilyl)benzene **3** was purchased from Gelest Inc. and recrystallized from diethyl ether/hexane. Diethyl ether and toluene were distilled from deep purple solutions of sodium benzophenone/ketyl. All other materials were reagent grade and used as received. The preparation of 1,4-dilithio-1,3-butadiyne was an adaptation from a literature procedure [19]. All thermal analysis experiments were carried out with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) at heating rates of 20 and 10 °C/min, respectively, and nitrogen flow rates of 100 cm^3/min. Infrared spectra were measured on a Nicolet Magna 750 FTIR spectrophotometer. ^1H and ^{13}C NMR spectra were acquired on a Bruker AC-300 spectrometer and referenced to the internal solvent peak. Molecular weight determination studies were performed using a Varian ProStar Model 410 autosampler and twin solvent delivery modules. Three Polymer Laboratories 10 μm Mixed B columns were used in series with a Polymer Laboratories PL-ELS 1000 light scattering detector using polystyrene as standard. THF was used as the solvent with a 1.0 ml/min flow rate.

2.2. Preparation of 1,4-bis(dimethylaminodimethylsilyl)butadiyne *2*

A flame dried 250 ml Schlenk flask containing diethyl ether (20 ml) was cooled to −78 °C and *n*-butyllithium (20 ml of 2.4 M in hexane, 48.0 mmol) was added by syringe. After several minutes, hexachlorobutadiene (1.88 ml, 12.0 mmol) was added drop-wise via syringe over a 10 min period. After completion of addition, the cold bath was removed and the mixture was stirred at room temperature for 3 h. The resulting 1,4-dilithio-1,3-butadiyne was used without further purification. The flask was then recooled to −78 °C and dimethylaminodimethylchlorosilane (3.6 ml, 24 mmol) was added by syringe. The flask was removed from the cold bath and the reaction mixture stirred at room temperature for 16 h. At this time, ^1H NMR analysis indicated the complete disappearance of dimethylaminodimethylchlorosilane and the formation of **2**. Diethyl ether was removed in vacuo, and the mixture was dissolved in a minimum amount of pentane and filtered. Pentane was removed in vacuo to give 2.91 g (96%) of **2**.

2.3. Preparation of silarylene–siloxane–diacetylene linear polymer *1*

A three-necked flask was equipped with a stir bar, reflux condenser, and inlet and outlet adapters for argon gas. The entire assembly was flame dried. 1,4-Bis(hydroxydimethylsilyl)benzene **3** (2.43 g, 10.7 mmol) was added to the flask. A previously prepared sample of 1,4-bis(dimethylaminodimethylsilyl)butadiyne, **2** (2.71 g, 10.7 mmol) was dissolved in 20 ml of toluene. This solution (16 ml) was added to the three-necked flask containing **3**. After refluxing the reaction mixture for 1 h, an incremental amount of the solution containing **2** (250–500 μl) was added at time intervals of 45 to 60 min until the viscosity of the solution had visibly increased and dimethylamine evolution had ceased, as determined by a moist litmus paper test on the exhaust stream of the argon outlet. ^1H NMR analysis indicated the disappearance of the starting materials and formation of **1**. Toluene was removed at reduced pressure and excess diethyl ether was added. The ether solution was washed with a saturated solution of aqueous NH_4Cl (2 × 100 ml). After aqueous workup and extraction with diethyl ether, the polymer solution was dried over anhydrous Na_2SO_4 and filtered. The solvent was removed in vacuo to give 2.71 g (65%) of **1** as a viscous brown liquid. IR (cm^{-1}) 2074 (s), (–C≡C–C≡C–), 1057 (vs, br), (Si–O). ^1H NMR ($CDCl_3$, ppm) 7.59 (s) C_6H_4, 0.39, 0.29, ($Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$, ppm) 140.39, 132.24, C_6H_4, 86.87, 85.34, (–C≡C–C≡C–), 2.00, 0.57, ($Si(CH_3)_2$). The weight-average molecular weight for **1** was about 10,000 g/mol.

2.4. Preparation of thermosetting plastic *4*

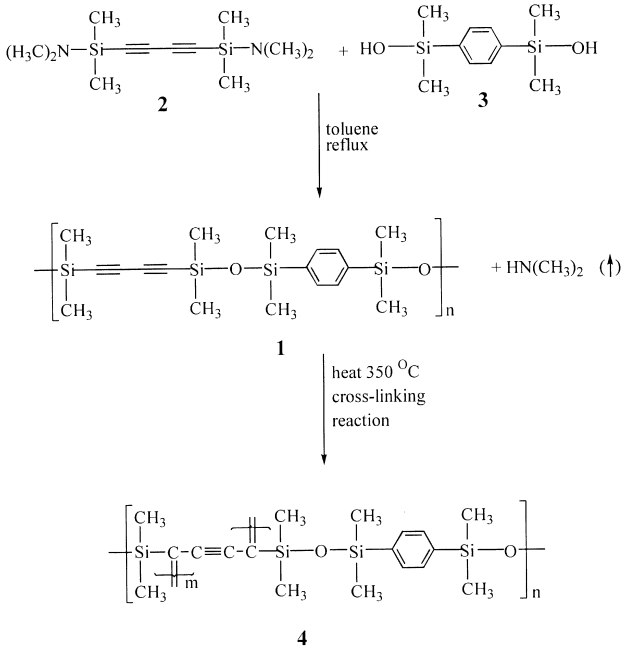
To a circular aluminum pan (pretreated with a teflon mold release) was weighed 1.2015 g of **1**. In order to remove any volatile material, the sample was heated at 125 °C under dynamic vacuum conditions for 2 h. Following the degassing procedure, the sample was placed in a tube furnace and cured under an atmosphere of dry argon for 2 h at 200, 250, 300, and 350 °C, respectively. After

completion of the curing cycle, the liquid linear poly(silarylene–siloxane–diacetylene) **1** had been transformed to a void-free, hard plastic disc.

3. Results and discussion

In order to incorporate a diacetylene unit into the silarylene–siloxane main chain, a synthetic route to the appropriate diacetylene containing monomer was required. Ijadi-Magsooke and Barton [19] have shown that 1,4-dilithio-1,3-butadiyne is readily prepared via a lithium–halogen exchange reaction between 4 equiv. of *n*-butyllithium and 1 equiv. of hexachlorobutadiene. Generation of this reactive species in situ followed by the addition of 2 equiv. of dimethylaminodimethylchlorosilane leads cleanly to the formation of 1,4-bis(dimethylaminodimethylsilyl)butadiyne **2**.

The linear polymer **1** was prepared by the aminosilane–disilanol polycondensation method. In this reaction, 1,4-bis(hydroxydimethylsilyl)benzene **3** is allowed to react with the difunctional-aminosilane **2**. Attack of the silanol oxygen on the silicon of the aminosilane occurs with the formation of the siloxane bond and the loss of dimethylamine gas (Scheme 1). Spectral data are consistent with the structure shown for **1**. A butadiyne stretch is present at 2074 cm^{-1} in the FTIR spectrum. Two signals at 86.87 and 85.34 ppm in the ^{13}C NMR spectrum are in the correct region for an internal butadiyne, which is substituted by $Si(CH_3)_2$ groups [13,20]. The absence of a stretching band in the FTIR spectrum around 3250 cm^{-1} (OH) and of a signal in the ^{1}H NMR spectrum around 2.44 ppm ($-N(CH_3)_2$) indicates that the starting materials have been consumed.



Scheme 1. Synthesis of thermosetting polymer **4**.

The presence of diacetylenic units in the backbone of linear polymer **1** provides sites for cross-linking purposes [12–17]. The diacetylenic moieties remain dormant under ambient conditions and the polymer must be heated to elevated temperature before conversion to a network system **4** is achieved. During reaction by thermal means, a conjugated cross-link is formed by an addition polymerization reaction without the formation or evolution of volatile byproducts.

3.1. Thermal properties

A strong exothermic signal is observed in the DSC thermogram (Fig. 1) for **1** peaking at 336 °C. This exothermic signal is typical of a cross-linking reaction between pairs of internal butadiyne groups [12–17,20]. A smaller signal peaking at 173 °C has been attributed to the cross-linking reaction between primary diacetylenic groups [21]. The primary (or terminal) diacetylenic group probably arises from reaction of gaseous dimethylamine with the alkynyl carbon–silicon bond in the growing polymer chain of **1**. Inspection of the ^{13}C spectrum for **1** reveals a weak signal in the correct region for terminal alkyne carbons [22], suggesting that some dimethylamine addition across the alkyne carbon–silicon bond has occurred. Kuwajima et al. [23] have shown that ethynyl silanes readily undergo nucleophilic substitution reactions at silicon. The presence of a terminal diacetylene group was also confirmed by the presence of weak absorptions in the FTIR spectrum centered at 2196, 2164, and 3314 cm^{-1}. These were attributed to the C≡C and ≡CH bonds, respectively, in the –SiC≡C–C≡CH units. The dimethylamine reaction would terminate chain growth and disrupt the alternating character of the polymer structure.

Heat treatment of linear polymer **1** for 2 h at 200, 250, 300, and 350 °C, respectively, resulted in a reaction between diacetylenic units producing cross-linked (networked)

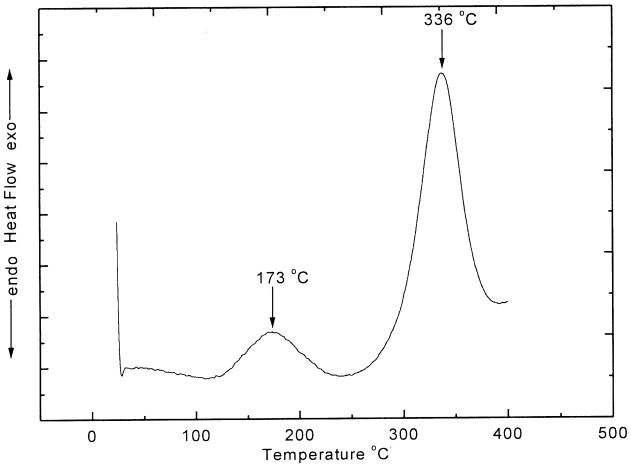


Fig. 1. DSC scan for **1** to 425 °C.

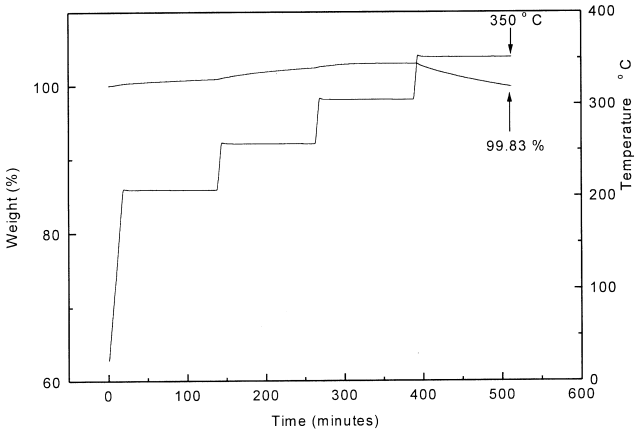


Fig. 2. Thermo-oxidative aging study on **4** for 2 h at 200, 250, 300, and 350 °C, respectively.

polymer **4** (Scheme 1). The networked polymer was completely insoluble in common organic solvents. FTIR analysis (KBr pellet) of **4** showed the complete absence of the diacetylenic-stretching band that was present at 2074 cm^{-1} in linear polymer **1**. A broad and very strong Si–O stretching band was observed at 1045 cm^{-1} indicating that under these conditions in an inert atmosphere the siloxane backbone remained intact. A strong and sharp band was present at 1270 cm^{-1} (Si–C) along with a band of medium intensity at 2963 cm^{-1} (aliphatic C–H stretching mode) indicating that the $Si–CH_3$ bonds also remained intact.

The thermal properties of cross-linked polymer **4** were determined by thermal analyses. A DSC scan on **4** from −70 to 400 °C at 40 °C/min showed the complete absence of the exothermic events assigned to the cross-linking reaction between terminal and internal diacetylenic units of linear polymer **1** and did not display a glass transition temperature. The thermal stability of **4** was determined using TGA by heating to 1000 °C at 10 °C/min under an atmosphere of dry nitrogen. The sample was stable with no weight loss up to 400 °C. The sample began to abruptly lose weight at around 425 °C with catastrophic degradation occurring to about 600 °C with a retention of 66% of the original weight. The weight loss had stabilized by 650 °C with a resulting char yield of 61% at 1000 °C.

3.2. Aging studies

In order to determine the long-term thermo-oxidative stability of cross-linked polymer **4**, aging studies were performed in a flow of air. Curing or conversion to a plastic material was accomplished by heating milligram quantities of liquid precursor **1** in the TGA chamber under an atmosphere of dry nitrogen. Curing of linear polymer **1** was achieved by heating for 1 h at 150 and 250 °C and for 2 h at 350 °C. Upon completion of the curing cycle, the sample was void-free and exhibited the characteristics of a plastic material. The thermosetting plastic **4** was allowed to cool to ambient temperature and then isothermally aged sequentially for 2 h at 150, 200, 250, 300, and 350 °C in air. During the heat treatment from 150 to 250 °C, the sample gained weight (2.8%) attributed to surface oxidation. Further heating at 300 and 350 °C resulted in a weight loss of 2.4 and 6.62%, respectively, or a final weight retention of 93.78%.

Another sample of linear polymer **1** was cured for 1 h at 150 and 250 °C and for 2 h at 350 and 440 °C, respectively. After curing to 440 °C, the FTIR spectrum of **4** was analogous to that described for linear polymer **1** cured to 350 °C. This indicates that the siloxane backbone remains intact even at 440 °C. After cooling to ambient temperature, the sample was isothermally aged sequentially for 2 h at 200, 250, 300, and 350 °C, respectively. The sample showed excellent thermo-oxidative stability (Fig. 2) exhibiting only a 0.17% weight loss. The increase in the curing cycle maximum temperature (350 °C versus 440 °C) results in a decrease in weight loss for cross-linked polymer **4** during aging. This could be directly attributed to the greater weight loss experienced during the curing cycle to 440 °C.

4. Conclusion

A linear silarylene–siloxane–diacetylene polymer was synthesized by an adapted version of the aminosilane-deficient method. It was determined that during the formation of linear polymer **1** some cleavage of the polymer occurred at the alkynyl carbon–silicon bond via dimethylamine reaction. This cleavage reaction disrupted the alternating nature of the polymer structure and hindered the formation of a truly high-molecular weight polymer. The linear polymer was thermally cross-polymerized through the diacetylene unit to produce a highly cross-linked plastic material. The cross-linking reaction was conveniently monitored by DSC and occurred at 173 °C for the primary diacetylene group and at 336 °C for the internal diacetylene unit. The cross-linked polymer began to thermally degrade above 400 °C in an inert atmosphere and was stable up to 350 °C in air.

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