Macromolecules **1994,** *27,* 4627–4628 **4627**

Regiospecific Head-to-Tail Ring-Opening Acetylene Metathesis Polymerization of Tetrasilacycloocta-3,7-diynes

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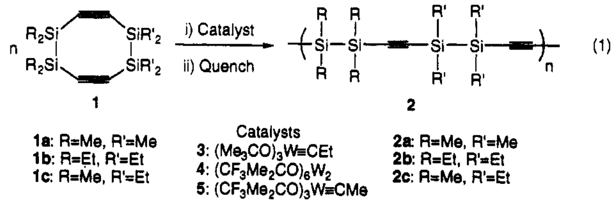
Received January 31, 1994
Revised Manuscript Received May 27, 1994

The recently reported poly(disilanyleneethynylene) (PDSE) materials contain structural features at the molecular level that are common to the two principal classes of conjugated polymers: π-conjugated polymers such as polyacetylene and σ-delocalized polysilanes. The polymer chain in these PDSE molecules consists of perfectly alternating disilanylene, $-Si(R)_2Si(R)_2-$, and acetylenic, $-C\equiv C-$, functionalities. Upon doping with SbF_5 vapor, films of these materials become conducting ($0.41–1.96\ S\cdot cm^{-1}$, depending on the nature of R).[1,2] It has been postulated that the conducting state results from donation of an electron from the silicon–silicon bond to the oxidizing agent and stabilization of the resulting charge by σ/π delocalization.[2b,3] Unlike many π-conjugated polymers the PDSE materials are soluble in common organic solvents and are stable to moisture and air. These properties allow convenient processability, an essential requirement for technological applications. Their stability and conducting properties make PDSE derivatives attractive candidates for study.

Two synthetic methods have previously been employed in the preparation of PDSE materials. The polymers were first prepared via anionic ring-opening polymerization of 1,2,5,6-tetrasilacycloocta-3,7-diynes using *n*-butyllithium. This procedure produces high molecular weight polymers (M_w in the range of 1×10^5; R = Ph, Et) but with a broad molecular weight distribution and in yields ranging from 35 to 90%. An alternate approach involves the condensation of 1,2-dichlorosilanes with dilithiated 1,2-diethynyldisilanes.[4]

We report herein a new ring-opening acetylene metathesis preparation of PDSE derivatives (eq 1). This process is metal-mediated and catalyzed by high-valent Schrock carbyne (alkylidyne) complexes of the type $(RO)_3W\equiv CR'$ ($RO = Me_3CO, CF_3Me_2CO$; $R' = Me, Et$).[5] The mechanism of this reaction is well understood and known to proceed via metallacyclobutadiene intermediates, the relative energetics of which have been well documented. Although the preparation of polymers containing carbon–carbon triple bonds in the backbone using these catalysts has been described,[6] the general applicability of this reaction has been restricted by the intrinsic instability characteristic of strained all-carbon cyclic acetylenes. For example, the half-life of cyclohexyne in CH_2Cl_2 is on the order of a few seconds at −110 °C.[7] The introduction of silicon atoms into rings containing the acetylene functionality increases stability substantially but does not prevent reaction with an electrophilic metal site. This reaction may be viewed as the triple bond analog of the ring-opening metathesis polymerization (ROMP) of cyclic olefins.[8]



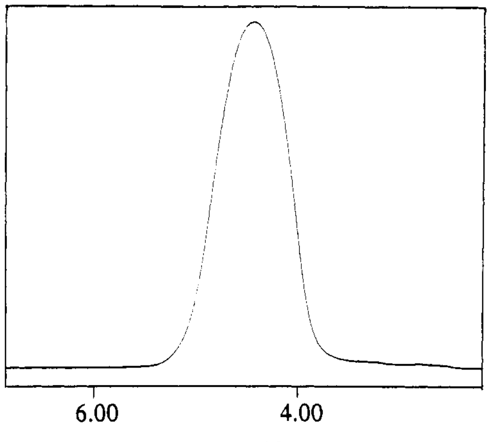


Figure 1. GPC of **2c** prepared using **4** (M_n = 31 000, PDI = 1.4, relative to polystyrene).

The reaction of **1a** with $(Me_3CO)_3W\equiv CEt$ (**3**) can be followed conveniently by ^1H NMR spectroscopy in C_6D_6 by monitoring the decrease of the H_β signal (3.85 ppm) of **3** and the corresponding appearance of a signal at 0.37 ppm characteristic of ring-opened **1a**.[9] Typically these reactions are sluggish; consumption of 5 equiv of **1a** using an initial alkylidyne concentration of 0.05 M requires over 30 h at 25 °C. Addition of 10 equiv of **1a** to **3** followed by quenching with methanol produces insoluble **2a** and oligomers.[10] Attempts to increase the molecular weight resulted in polymer precipitation before complete monomer consumption. The low solubility of **2a** has been previously attributed to polymer crystallinity and appears to be independent of the preparation method.[11]

Finally, the reactivity of **1a** with the triply bonded dimer $W_2(OCMe_2CF_3)_6$ (**4**) was tested since it is known that certain acetylenes can cleave the tungsten–tungsten triple bond, in a metathesis-like reaction, to produce two alkylidyne species.[12] Addition of 3 equiv of **1a** to **4** in C_6D_6 results in complete monomer consumption over 3 h at 25 °C, producing soluble oligo-**1a** (M_n = 5200) along with insoluble **2a**. The rate of **1a** consumption in this reaction is qualitatively much faster than that of **4**; hence, the propagation rate is faster than the initial cleavage of the tungsten–tungsten triple bond in **4**.

In view of the insolubility problems associated with **2a**, efforts were directed toward the preparation of **2b**. Neither **3** nor **4** reacts with the acetylene functionality in **1b**, even under forcing conditions. Quantitative polymerization of **1b** was ultimately achieved, by the *in situ* generation of $(Me_2(CF_3)CO)_3W\equiv CCH_3$ (**5**), an initiator that is more electrophilic than **3** and is sterically less hindered than **4**. For example, reaction of 10 equiv of **1b** with **5**, prepared by addition of 1.2 equiv of 2-butyne to $W_2(OCMe_2CF_3)_6$,[13] yields **2b** with M_n = 4300 and PDI = 1.4. These observations clearly underscore the acute sensitivity to electronic and steric influences of the substrate–catalyst interaction.

We postulated that the discriminatory nature of the catalyst could be exploited to induce the regiospecific polymerization of **1c**.[14] This monomer contains two disilane functionalities that differ only in the size (Me vs Et) of the substituents on silicon and should preferentially form one of two possible metallacyclobutadiene intermediates according to the catalyst–monomer reactivity described for **1a** and **1b**. This selectivity should ultimately

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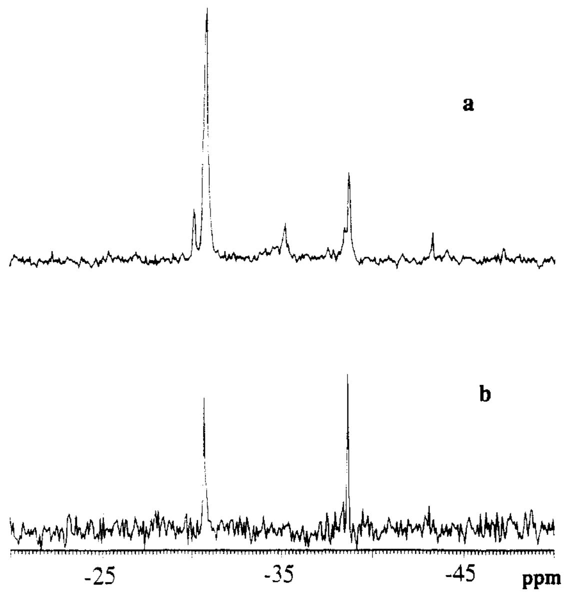
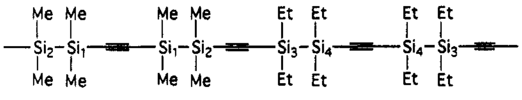


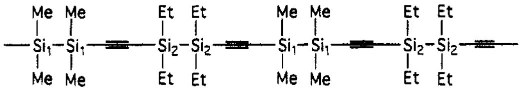
Figure 2. (a) ^{29}Si NMR spectrum of **2c** in $CDCl_3$ prepared anionically using $LiCH_2SiMe_3$. (b) ^{29}Si NMR spectrum of **2c** in $CDCl_3$ prepared using **4**.

lead to a stereoselective head-to-tail polymerization. Indeed, this is the observed reactivity when **1c** is polymerized using initiator **4** to yield soluble **2c** (M_n = 31 000, PDI = 1.4; Figure 1) as determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (Figure 2).[15] The observation of only *two* signals in the ^{29}Si NMR spectrum was critical to the assignment of a head-to-tail configuration (**A**). It is important to note that a regiospecific head-to-head sequence (**B**) would give rise to *four* signals. The ^{29}Si NMR spectrum of a nonregiospecific polymer obtained by polymerization of **1c** initiated with Me_3SiCH_2Li is shown in Figure 2 for comparison.[16]



$-\underset{Me}{\overset{Me}{Si_2}}-\underset{Me}{\overset{Me}{Si_1}}\equiv\underset{Me}{\overset{Me}{Si_1}}-\underset{Me}{\overset{Me}{Si_2}}\equiv\underset{Et}{\overset{Et}{Si_3}}-\underset{Et}{\overset{Et}{Si_4}}\equiv\underset{Et}{\overset{Et}{Si_4}}-\underset{Et}{\overset{Et}{Si_3}}\equiv$

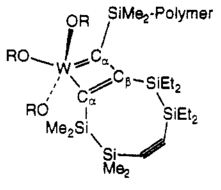
B



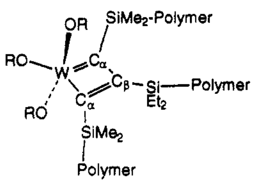
$-\underset{Me}{\overset{Me}{Si_1}}-\underset{Me}{\overset{Me}{Si_1}}\equiv\underset{Et}{\overset{Et}{Si_2}}-\underset{Et}{\overset{Et}{Si_2}}\equiv\underset{Me}{\overset{Me}{Si_1}}-\underset{Me}{\overset{Me}{Si_1}}\equiv\underset{Et}{\overset{Et}{Si_2}}-\underset{Et}{\overset{Et}{Si_2}}\equiv$

A

Results described herein demonstrate that the acetylene metathesis route provides an efficient alternative to anionic and condensation procedures for the preparation of this class of materials. Although the molecular weight distributions of the polymers are narrower than those produced via other methods, their values suggest that some chain transfer (i.e., secondary metathesis) occurs during the time scale of the polymerization. The regiospecific generation of **2c** by **4** demonstrates nicely the ability of carefully chosen transition-metal reagents to assemble organic fragments into a controlled polymeric sequence. It is reasonable to postulate that propagation in the polymerization of **1c** proceeds selectively via **C**, one of the two possible metallacyclobutadiene intermediates. Such a disposition of substituents places the bulkier $SiEt_2$ substituent on C_β and away from the sterically congested metal. Since there is evidence that secondary metathesis may be occurring to a small extent during polymerization, this step must be stereospecific as well, and we postulate that it proceeds through metallacyclobutadiene **D**.



C



D

Studies are currently underway to ascertain the difference in reactivity toward the tungsten center between the acetylenic functionality in the monomer and that in the polymer. This information will be important in determining whether a living polymerization system can be achieved using these catalysts.

Acknowledgment. The authors gratefully acknowledge the University of Rochester and NSF (CHE-9120001) for partial support of this work. G.C.B. thanks the Dreyfus Foundation for a Distinguished New Faculty Award.

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(9) All polymerizations were carried out inside a nitrogen-filled glovebox using rigorously dried glassware and solvents. See: *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.

(10) Identified as **2a** by comparison to previously characterized samples in refs 2b and 4.

(11) It seems that, according to results in ref 4, **2a** is slightly more soluble in polar solvents such as tetrahydrofuran and dichloromethane. However, the reactivity of the catalysts is attenuated in these solvents, resulting in little or no monomer conversion. There are no reports of soluble **2a** of $M_w > 10^4$ (vs polystyrene standards).

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(14) Preparation of **1c**: Deprotonation of $HC{\equiv}CSiMe_2SiMe_2C{\equiv}CH$ (1.44 g, 8.9 mmol) in THF (25 mL) proceeds smoothly by dropwise addition of EtMgCl (18 mmol in THF). The resulting mixture was stirred at room temperature for 2 h, treated with $ClSiEt_2SiEt_2Cl$ (1.9 g, 8.3 mmol) in THF (12 mL), and allowed to stir for an additional 6 h. After removal of solvent the residue was treated with hexane (100 mL) and 25 mL of 10% NH_4Cl. The organic phase was washed twice with water and dried with $MgSO_4$. Removal of solvent and fractional distillation (70–80 °C, 0.04 Torr) gives 1.6 g (55%) of **1c** as a clear viscous liquid that solidifies upon standing: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (t, $SiCH_2CH_3$, 12), 0.72 (m, $SiCH_2CH_3$, 8), 0.19 (s, $SiCH_3$, 12); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.5 ($Et_2SiC{\equiv}CSiMe_2$), 118.5 ($Et_2SiC{\equiv}CSiMe_2$), 8.72 ($SiCH_2CH_3$), 4.75 ($SiCH_2CH_3$), −3.0 ($SiCH_3$).

(15) Typical polymerization: In a nitrogen-filled glovebox a solution of **1c** (250 mg, 0.74 mmol) in toluene (1.0 mL) was added to **4** (10 mg, 0.01 mmol) in toluene (10 mL) and the resulting solution was stirred at 25 °C for 10 days. Quenching with $PhC{\equiv}CMe$ and precipitation by addition of the resulting solution to methanol yields **2c** as a white powder which is isolated by centrifugation (215 mg, 86%): M_n = 31 000, PDI = 1.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, 12), 0.73 (q, 8), 0.23 (s, 12); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.7 ($C{\equiv}CSi(Et)_2$), 113.3 ($C{\equiv}CSi(Et)_2$), 8.5 ($SiCH_2CH_3$), 5.0 ($SiCH_2CH_3$), −2.9 ($SiCH_3$); ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −38.62, −30.7.

(16) Prepared via a procedure similar to that described in ref 2a.