

Germanium-containing polymers via acyclic diene metathesis

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Abstract

The synthesis of unsaturated polycarbogermanes via acyclic diene metathesis (ADMET) polymerization is reported. Exposure of germanadienes to well-defined olefin metathesis catalysts yields unsaturated polymers containing germanium along the backbone in a clean process. The polymers are viscous liquids with glass transition temperatures around -90°C . Thermogravimetric analysis suggests a non-volatile residue after thermal decomposition, possibly elemental germanium. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: ADMET polymerization; Organometallic polymers; Olefin metathesis; Germanium

1. Introduction

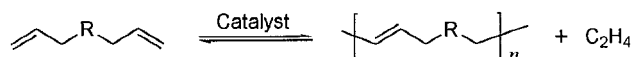
The synthesis of organometallic polymers (or metal-polymers) has become an extensively investigated and fruitful new discipline, and has emerged as a possible route towards materials exhibiting unique properties arising from both the metallic and the organic components [1]. Among the numerous combinations of structures and properties available today, metalpolymers obtained through the polymerization of monomers containing a covalent metal–carbon bond still represent a relatively small portion [2]. This is a clear representation of the marked stability of chelate and in general, coordination complexes with respect to covalent structures, as well as the many possibilities offered by coordination chemistry in terms of oxidation states, ligand combinations, and metal incorporation. Such advantages have been creatively explored in strategies where the propagation reaction involves coordination phenomena [2].

Several groups have proven the utility of organometallic polymers of Group 14 elements because of their thermal and optical behavior [3]. Among these, germanium-based polymers have demonstrated potential utility in microlithography [4] and in the preparation of ceramic materials [5]. The availability of novel,

well defined polymeric structures involving polycarbogermanes is of utmost importance for the development of precise applications of this type of materials.

The synthesis of covalent metalpolymers using acyclic diene metathesis (ADMET) chemistry is today an area of considerable interest to us. ADMET polymerization is a transition metal-catalyzed step polycondensation producing an unsaturated polymer from α,ω -dienes in an equilibrium process, which is driven to completion by the removal of the condensate [6]. (Scheme 1) Well-defined alkylidene catalysts such as **1** or **2**, as well as classical metathesis catalysts derived from tungsten aryloxides, have proven useful in ADMET chemistry (Fig. 1) [7].

Continuing research efforts within our group and others have been devoted to elucidating the rules that govern diene structure–reactivity, to studying the compatibility between catalysts and polymerizable dienes, and finally, to exploring novel catalytic systems which would expand these possibilities. These investigations have provided access to polymers containing a wide variety of functionalities incorporated within the main chain following essentially the same polymerization protocol [8].



Scheme 1. Acyclic diene metathesis (ADMET) polymerization.

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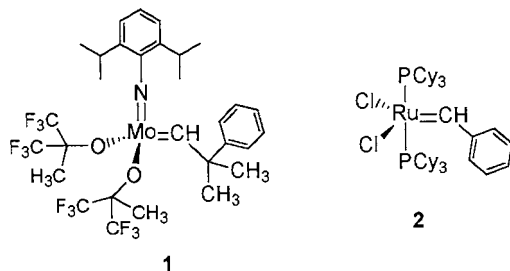


Fig. 1. Two well-defined olefin metathesis catalysts.

Polymers containing silicon and tin have been efficiently synthesized via ADMET [9,10], and in the case of tin, compositions containing up to 46% metal have been synthesized in our hands. Furthermore, tin-containing dienes can be polymerized with the well-defined molybdenum catalyst **1**, as well as with tungsten-based precatalysts for classical systems acting, in the latter case, as both monomer and precatalyst activator [10a,b].

In this paper we report the results of our investigations on the synthesis of main chain germanium-containing polymers via the ADMET polymerization of germanadienes. Among the many germanium-containing polymers known today [11], the cyclopolymerization of dipropargylgermaniums [12] and the ring opening metathesis polymerization of germanium-functionalized cycloolefins [13] are previous examples of metathesis polymerization of germanium-containing monomers. ADMET polymerization should prove useful in the preparation of unsaturated homo- and copolymers of germanium-based monomers, yielding linear structures which can be subject to further functionalization, either through the derivatization of the olefin moiety present in each repeat unit, or through the design of telechelic oligogermanes and their incorporation in more complex polymer architectures. Particularly, the synthesis of segmented copolymers containing a soft organometallic and a hard organic phase, as well as the preparation of organometallic, polymeric precursors to ceramic materials constitute a continuous ongoing effort within our research group.

2. Experimental

2.1. General

All manipulations were performed following either standard Schlenk, high vacuum line, or drybox techniques. Diethyl ether was distilled from sodium benzophenone ketyl, while alkenyl halides were purified by vacuum distillation from calcium hydride. The olefin metathesis catalysts $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NC}_6\text{H}_3\text{Pr}_2)(\text{OC}(\text{CF}_3)_2\text{Me})_2$ (**1**) and $\text{Cl}_2\text{Ru}(\text{CHPh})(\text{PCy}_3)_2$ (**2**) were syn-

thesized following the literature methods [14,15]. ^1H - (300 MHz) and ^{13}C -NMR (75 MHz) spectra were run in a Varian VXR-300 superconducting system in CDCl_3 , and are referenced to internal tetramethylsilane. A pulse sequence with gated decoupling and 20 s delay time was employed for quantitative ^{13}C -NMR analysis. Gel permeation chromatography analyses were performed in a Waters Associates model 590 chromatograph using chloroform as the eluent (1.0 ml min^{-1}), and are based on calibration with polystyrene standards. High resolution EI, CI and LSI MS analyses were performed in a Finnigan MAT95Q hybrid sector mass spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA). Thermogravimetric analysis was performed in a Perkin-Elmer TGA7 instrument in the range $100\text{--}800^\circ\text{C}$ at a heating rate of $20^\circ\text{C min}^{-1}$ under an N_2 atmosphere. Differential scanning calorimetry was performed in a Perkin-Elmer DSC7 instrument at a heating/cooling rate of $20^\circ\text{C min}^{-1}$ in the range of -110 to 0°C .

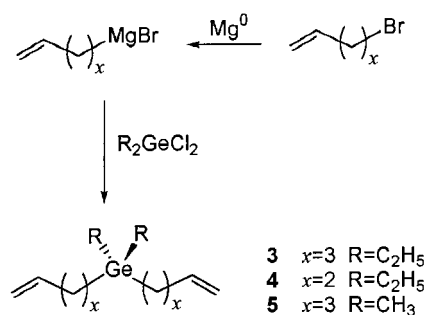
2.2. Monomer synthesis

2.2.1. Synthesis of bis(4-pentenyl)-diethylgermanium (**3**): (6,6-diethyl-6-germana-1,10-undecadiene)

A flame-dried round bottom flask was adapted with a reflux condenser and an addition funnel. Magnesium powder (2.17 g, 89.3 mmol) was suspended in ca. 40 ml anhydrous diethyl ether, and a solution of 5-bromo-1-pentene (10.7 g, 71.4 mmol) in ether (25 ml) was added to the Mg suspension at a rate at which spontaneous reflux was obtained. The Grignard reagent solution was refluxed for an additional hour and cooled to room temperature (r.t.), prior to the slow addition of a solution of diethylgermanium dichloride (4.80 g, 23.8 mmol) in 25 ml ether. The resulting reaction mixture was refluxed for ca. 24–30 h, cooled to r.t. and carefully poured over ice-cold 1 M NH_4Cl . Extraction with ether, drying over MgSO_4 and removal of the solvent in vacuo, yielded a pale yellow liquid. Further purification by vacuum fractional distillation, followed by vacuum transfer from CaH_2 afforded 5.17 g (89%) of pure **3**. ^1H -NMR δ (ppm) = 5.80 (ddt, 2H, $\text{CH}_2=\text{CH}$); 4.95 (dd, 4H, $\text{CH}_2=\text{CH}$); 2.05 (dt, 4H, $\text{CH}-\text{CH}_2$); 1.43 (m, 4H, $\text{CH}_2-\text{CH}_2-\text{CH}_2$); 1.00 (t, 6H, CH_3); 0.65–0.74 (8H, $\text{Ge}-\text{CH}_2$). ^{13}C -NMR δ (ppm) = 138.9 ($\text{CH}_2=\text{CH}$); 114.4 ($\text{CH}_2=\text{CH}$); 37.8 ($\text{CH}-\text{CH}_2$); 24.7 ($\text{CH}_2-\text{CH}_2-\text{CH}_2$); 11.5 ($\text{CH}_2-\text{CH}_2-\text{Ge}$); 9.0 (CH_3); 4.3 (CH_2-CH_3). HR MS: $(\text{M}-1)^+ = 271.1445$; 241 ($\text{C}_{12}\text{H}_{23}\text{Ge}$) 72%; 201 ($\text{C}_9\text{H}_{19}\text{Ge}$) $^+$ 100%. Anal. Calc. for $\text{C}_{14}\text{H}_{28}\text{Ge}$: H, 10.49; C, 62.52. Found: H, 10.61; C, 62.36%.

2.2.2. Cognate synthesis of bis(3-butenyl)-diethylgermanium (**4**): (5,5-diethyl-5-germana-1,8-nonadiene)

Diene **4** was prepared following the procedure described above. Yield: 77%. ^1H -NMR δ (ppm) = 5.95



Scheme 2. Synthesis of monomers 3–5 from the corresponding dialkylgermanium dichloride.

(ddt, 2H, $CH_2=CH$); 4.95 (dd, 4H, $CH_2=CH$); 2.10 (dt, 4H, $CH-CH_2$); 1.05 (t, 6H, CH_3); 0.90–0.60 (8H, $Ge-CH_2$). ^{13}C -NMR δ (ppm) = 141.6 ($CH_2=CH$); 112.8 ($CH_2=CH$); 29.3 ($CH-CH_2$); 11.1 (CH_3); 8.9 (CH_2-CH_3); 4.4 (CH_2-CH_2-Ge). HR MS: $(M-1)^+$ = 241.0953; 213 ($C_{10}H_{19}Ge$) 25%; 197 ($C_9H_{17}Ge$) 53%; 187 ($C_8H_{17}Ge$) 100%; 185 ($C_8H_{15}Ge$) 73%; Anal. Calc. for $C_{12}H_{24}Ge$: H, 10.04; C, 59.83. Found: H, 10.26; C, 59.67%.

2.2.3. Cognate synthesis of bis(4-pentenyl)-dimethylgermanium (5): (6,6-dimethyl-6-germana-1,10-undecadiene)

Diene 5 was prepared following the procedure described above. Yield: 55%. 1H -NMR δ (ppm) = 5.89 (ddt, 2H, $CH_2=CH$); 4.95 (dd, 4H, $CH_2=CH$); 2.04 (dt, 4H, $CH-CH_2$); 1.44 (m, 4H, $CH_2-CH_2-CH_2$); 0.70 (m, 4H, $Ge-CH_2$); 0.07 (s, 6H, $Ge-CH_3$). ^{13}C -NMR δ (ppm) = 138.9 ($CH_2=CH$); 114.4 ($CH_2=CH$); 37.5 ($CH-CH_2$); 24.6 ($CH_2-CH_2-CH_2$); 15.0 (CH_2-CH_2-Ge); -4.2 (CH_3-Ge). HR MS: $(M-1)^+$ = 241.1019; 227 ($C_{11}H_{21}Ge$) 26%; 173 ($C_7H_{15}Ge$) 100%. Anal. Calc. for $C_{12}H_{24}Ge$: H, 10.04; C, 59.83. Found: H, 10.55; C, 57.83%.

2.3. Polymer synthesis

2.3.1. ADMET polymerization of diene 3: synthesis of polymer 6

Monomer 3, (1.00 g, 3.72 mmol) and catalyst 1 (12 mg, ca. 16 μ mol) were weighed in an argon-purged drybox and placed into a 25 ml round bottomed flask equipped with a Teflon™ high vacuum valve and a stir bar. The flask was stirred for 5 min in the box, sealed, and taken to a high vacuum Schlenk line, where the reaction mixture was stirred for ca. 48 h (or until ethylene evolution stopped). Polymerization was terminated by exposing the flask contents to the atmosphere. The crude polymer was taken up in $CDCl_3$ and precipitated from ice-cold methanol. The viscous liquid was dried under vacuum for 24 h. Attempts to remove

catalyst residues by dissolution in $CHCl_3$ followed by filtration through different adsorbents (silica gel, alumina and activated charcoal) were fruitless. Yield: 82%. 1H -NMR δ (ppm) = 5.40 (2H); 2.00 (4H); 1.42 (4H); 1.00 (t, 6H); 0.74 (8H). ^{13}C -NMR δ (ppm) = 130.4 (olefin, *trans*), 129.8 (olefin, *cis*), 36.6 (allylic, *trans*), 31.3 (allylic, *cis*), 25.4, 11.6, 9.0, 4.4. M_n (GPC) = 14 800, M_w/M_n (GPC) = 1.79. T_d (TGA, onset) = 299°C. $T_{10\%}$ (TGA) = 353°C. T_g (DSC) = -89°C. Anal. Calc. for $(C_{12}H_{24}Ge)_n$: H, 10.04; C, 59.83. Found: H, 9.91; C, 59.36%.

2.3.2. Cognate polymerization of diene 4: synthesis of polymer 7

Diene 4 was polymerized following the procedure described above. Polymer 7 was not purified prior to characterization. Yield: 91%. 1H -NMR δ (ppm) = 5.42, 5.30 (2H); 2.05 (4H); 1.00 (4H); 0.65–0.85 (8H). ^{13}C -NMR δ (ppm) = 131.6 (olefin, *trans*), 131.3 (olefin, *cis*), 28.0 (allylic, *trans*), 22.6 (allylic, *cis*), 11.9, 9.0, 4.5. M_n (GPC) = 18 000, M_w/M_n (GPC) = 1.42. T_d (TGA, onset) = 428°C. $T_{10\%}$ (TGA) = 428°C. T_g (DSC) = -98°C. Anal. Calc. for $(C_{10}H_{20}Ge)_n$: H, 9.47; C, 56.43. Found: H, 9.33; C, 55.80%.

2.3.3. Cognate polymerization of diene 5: synthesis of polymer 8

Diene 5 was polymerized following the procedure described above, but using catalyst 2. Yield: 75%. 1H -NMR δ (ppm) = 5.38 (2H); 2.01 (4H); 1.37 (4H); 0.60–0.80 (4H); 0.04 (s, 6H). ^{13}C -NMR δ (ppm) = 130.4 (olefin, *trans*), 129.8 (olefin, *cis*), 36.4 (allylic, *trans*), 31.0 (allylic, *cis*), 25.4, 25.3, 15.3, 15.1, -4.0, -4.2. M_n (GPC) = 5300, M_w/M_n (GPC) = 2.31. T_d (TGA, onset) = 244°C. $T_{10\%}$ (TGA) = 290°C. T_g (DSC) = not observable. Anal. Calc. for $(C_{10}H_{20}Ge)_n$: H, 9.47; C, 56.43. Found: H, 9.21; C, 56.10%.

3. Results and discussion

The incorporation of different functional groups in ADMET polymers is the outcome of an appropriate monomer design, a process which often comprises a study not only in functionality–catalyst compatibility, but also in the prediction of the polymer properties based on the structure of the parent diene. Because of the interesting physical and chemical properties exhibited by a series of polycarbostannanes made via ADMET [10], we have turned our attention to organometallic polymers containing germanium.

The synthesis of germanadiene monomers can be achieved with relative ease. The parent dialkylgermanium dichloride is used as the starting material, and moderate to good yields are obtained in a straightfor-

Table 1
Characterization data for polymers 6–8

Polymer	Catalyst ^a	M_n ^b	PDI ^b	$T_{10\%}$ ^c (°C)	Residual wt% ^c	T_g ^d (°C)	% <i>trans</i> ^e
6	1	14 800	1.79	353	17	–89	71
7	1	18 000	1.42	428	8	–98	84
8	2	5300	1.82	290	3	–	73

^a All polymerizations run at 0.4% mol catalyst in neat monomer.

^b Determined by GPC in CHCl_3 using polystyrene standards.

^c Determined by TGA.

^d Determined by DSC.

^e Determined by integrating the *trans* and *cis* olefin signals in the quantitative ^{13}C -NMR.

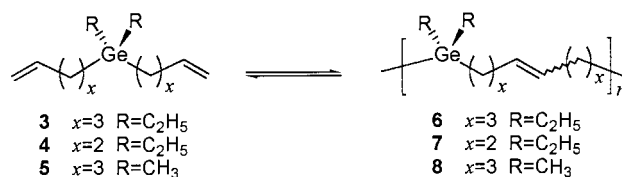
ward Grignard reaction. (Scheme 2) Careful purification of monomers 3–5 (>99.5% purity by GLC) involves fractional distillation, drying over CaH_2 and vacuum transfer followed by several freeze–pump–thaw cycles. Monomers 3–5 were characterized by ^1H -NMR, ^{13}C -NMR, and MS, and gave satisfactory elemental composition data.

When exposed to catalysts 1 or 2 (0.4 mol%, see Table 1), monomers 3–5 condense to high molecular weight polymers in a clean olefin metathesis process. (Scheme 3) Ethylene evolution is indicated by a constant bubbling throughout the polymerization, while a steady increase in viscosity suggests an increase in degree of polymerization in good agreement with a step polymerization scheme [16]. After 24–36 h of reaction, magnetic stirring of the reaction mixture becomes impossible and an increase in the reaction temperature (up to 60°C) usually contributes to achieving higher molecular weight. After 48–72 h, no apparent evolution of ethylene is observed and the polymerization is terminated by exposing the contents of the reaction mixture to the atmosphere.

Polymers 6–8 are viscous liquids, readily soluble in toluene, CHCl_3 , and CH_2Cl_2 , but virtually insoluble in other conventional organic solvents. The chemical structure of polymers 6–8 is confirmed by examining the ^1H - and ^{13}C -NMR spectra, which reveal the expected structure of linear unsaturated polycarbogermanes. Integration of the two olefin signals in the quantitative ^{13}C -NMR (e.g. 130.4 and 129.8 ppm for 6), shows that the polymers contain mainly *trans* linkages (ca. 71–84%, see Table 1) between repeat units, an observation consistent with many other ADMET polymers which agrees with the relative stability of the *trans* and *cis* isomers formed in an equilibrium process. The ^{13}C -NMR of polymer 6 is shown in Fig. 2. Both ^1H - and ^{13}C -NMR suggest a high degree of polymerization for 6 and 7 since the signals corresponding to terminal olefin (due to end-groups) are either not observable or of very low intensities. Low signal-to-noise ratio for such signals prevents an estimation of the number

average molecular weight of the polymers by end-group analysis. However, in the case of polymer 8, although a high molecular weight is suggested by both ^1H - and ^{13}C -NMR, the presence of other unassigned, low intensity signals in the olefin region of the ^{13}C -NMR may be an indication of either the formation of cyclic oligomers or to partial isomerization of the terminal double bonds. This behavior is also supported by the larger polydispersity as well as the difference with the calculated M_n obtained from chromatographic analysis. Molecular weight determination by gel permeation chromatography in CHCl_3 (polystyrene standards) shows that high molecular weight ($M_n = 18\,000$ and $14\,000\text{ g mol}^{-1}$, respectively) can be achieved for polymers 6 and 7, while a lower molecular weight is found for 8 (ca. 5300). We are currently exploring the factors that determine an apparent decreased reactivity of monomer 5 towards the metathesis catalysts employed in our study.

Thermal analysis reveals some of the most interesting features of the germanium-containing polymers described herein. Thermogravimetric analysis (TGA) shows that polymers 6–8 are stable up to 250°C, the temperature at which thermal decomposition begins (Table 1 lists the 10% weight reduction temperatures, $T_{10\%}$). TGA also shows 17% weight recovery after heating a sample of polymer 6 to 800°C under an N_2 atmosphere, while the residual material in the case of polymers 7 and 8 is 8 and 3%, respectively. These residues may be attributed to elemental germanium by analogy to the behavior exhibited by ADMET polycarbostannanes, but no definitive determination of the



Scheme 3. ADMET synthesis of polymers 6–8.

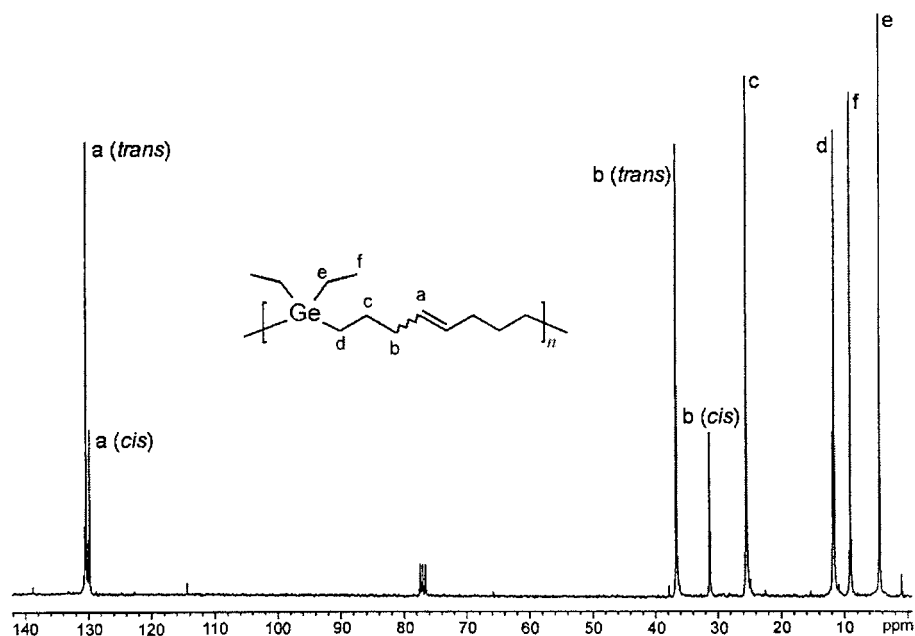


Fig. 2. ^{13}C -NMR (75 MHz, CDCl_3) spectrum of polymer 6.

chemical identity of this product has been made. Although the metal recovery is not quantitative (e.g. the expected metal content in **6** is ca. 29%), potential applications of these materials could be based in this behavior. The TGA traces for the three polymers are shown in Fig. 3.

Differential scanning calorimetry (DSC), in turn, shows that polymers **6–8** are completely amorphous. No melting temperatures could be observed in the range -110 to 0°C , while a glass transition can be found at -89 and -98°C for **6** and **7**, respectively (Fig. 4). The combined characterization data is summarized in Table 1.

The structure–reactivity rules that govern the AD-MET polycondensation of germanium-containing dienes still seem unclear to us. For example, attempts to synthesize polymer **8** using Schrock's molybdenum alkylidene **1** turned futile. However, this observation may not reflect a true chemical behavior but an improper choice of experimental conditions and we are currently trying to expand on this study. Another interesting observation arising from the thermal behavior of polymers **6–8** is the fact that the % weight recovered in TGA analysis does not correspond to the theoretical weight–metal content, as is the case for analogous tin-containing polymers. Such an observation can be rationalized by appealing to the formation of more volatile species in the case of germanium, or to the presence of different decomposition pathways for the two types of polymers. We are currently devoted to the synthesis of other germanium-containing species, espe-

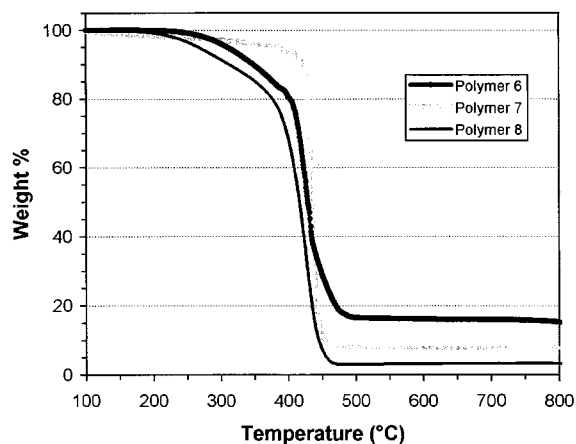


Fig. 3. TGA traces for polymers **6–8**.

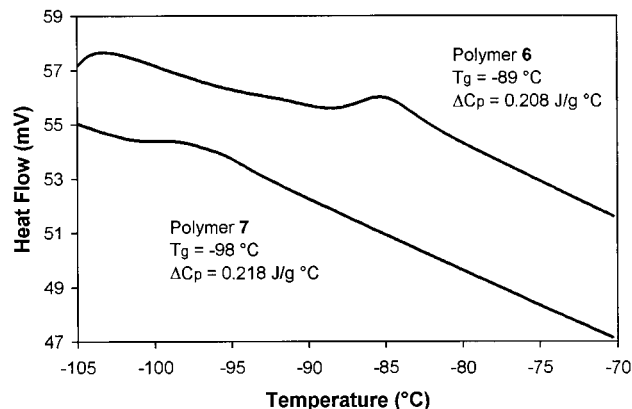


Fig. 4. Partial DSC traces for polymers **6** and **7**.

cially telechelic oligogermane dienes which could exhibit interesting properties imparted by the presence of Ge–Ge bonds along the polymer backbone.

In comparison to other ADMET metallopolymers, polymers **6–8** exhibit a similar pyrolysis behavior than the observed for the tin-containing analogues, although the extent of metal recovery is lower. Analogously, DSC analysis of the polycarbostannanes synthesized in our laboratories reveal very low glass transition temperatures (ca. -90°C and lower), as well as amorphous character. This observation has led us to believe that the conformation of the polymers (due to the identity of the side chains and the geometry of the heteroatom) is not only likely to be the same, but also the determining factor of the thermal properties of these two families of polymers. A comparison to the analogous ADMET polycarbosilanes is more difficult because of the structural differences between the two groups of polymers studied. In a fashion that resembles their Sn and Ge analogues, all homopolymers synthesized from aliphatic siladienes seem to be amorphous (DSC), and crystallinity is only introduced either by copolymerization with hydrocarbon monomers such as 1,9-decadiene [9a], or by the incorporation of aromatic moieties in the backbone [17]. However, a marked difference is observed in their pyrolysis behavior since no silicon residue is found when the materials are decomposed under a nitrogen atmosphere [9a]. This feature suggests that derivatization procedures may be necessary to improve the ceramic yield of the Si- and Ge-based materials. ADMET copolymerization of organometallic dienes should provide access to ceramic precursors in which the elemental composition is determined by the stoichiometric ratio of the comonomer units, and this application is currently an area of significant interest to us.

4. Conclusion

Polycarbogermanes can be synthesized via ADMET chemistry catalyzed by Schrock's molybdenum alkylidene **1** or by Grubbs' ruthenium carbene **2**, expanding the scope of ADMET polymerization to include novel organometallic structures. High molecular weight unsaturated polymers can be obtained in a clean metathesis polycondensation process. The polycarbogermanes obtained are viscous liquids which contain up to 34% metal weight, with number average molecular weights ranging from 5000 to 18 000 g mol^{-1} . ADMET copolymerization can provide access to novel polymeric structures with promising physical properties. The synthesis of other covalent and coordination metal-containing polymers, as well as the synthesis of mixed-metal-con-

taining polymers are areas under active exploration within our research group.

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