

Synthesis and characterization of Ge- and Sn-containing ADMET polymers

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Abstract

A series of dienes containing the germanium and tin moiety were synthesized and their acyclic diene metathesis (ADMET) polymerization was investigated in the presence of electrochemically reduced tungsten-based catalyst system. All monomer and polymer structures were characterized by ^1H and ^{13}C NMR spectroscopy. Average molecular weights are determined by GPC. Glass transition temperatures of polymers were determined by DSC. The results in this work are comparing with those obtained by the other catalyst systems.

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1. Introduction

Organometallic polymers have emerged as an important category of the new materials in the past decades. The interest in developing these materials resulted from the fact that incorporation of transition metals into polymer structure allows access to materials with unusual and attractive characteristics including electrical, magnetic and optical effects [1–7]. The field of organometallic polymers is still rather underdeveloped and there is great potential in combining the attributes of flexibility, versatility and solubility of the organic groups with the magnetic, electrical and optical properties of the metal. Among the numerous combinations of structures and properties available today, metallopolymers obtained through the polymerization of monomers containing a covalent metal–carbon bond still represent a relatively small portion. 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 [8].

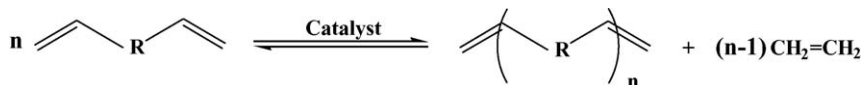
Organometallic polymers are well-known materials made by a variety of techniques [9]. Examples of polymeric materials incorporating tin have been in the literature since the

1960s [10–12]. The polymerization of olefins such as tin acrylates is the most common route to tin-containing polymers, and this specific example has become a widely used approach towards polymeric biocides. The first examples of polycarbostannane polymers were synthesized via step polymerization of diolefins (or diacetylenes) and tin dihydrides. Another interesting example of tin-containing polymers are synthesized from tin-containing α,ω -dienes and metal or aryl dihalides [13]. As demonstrated by Cummins, ring opening metathesis polymerization can also be a route towards organometallic polymers synthesized from norbornene and norbornene-type metal chelates [14]. Many germanium-containing polymers known today [15–20]. The first synthetic scheme towards germanium-containing polymers to involve the metathesis reaction was reported by Cho et al. [21]. The ring opening metathesis polymerization (ROMP) of germanium-functionalized cycloolefins [22] are previous example of germanium-containing monomers polymerized by metathesis chemistry.

Acyclic diene metathesis (ADMET) polymerization is also a valuable tool for the synthesis of unsaturated metal containing polymers such as polycarbogermans and polycarbostannes [23,24]. ADMET polymerization, the condensation of terminal dienes to yield high polymer, has been found to be an extremely versatile reaction (Scheme 1).

Ge- and Sn-containing unsaturated ADMET polymers were synthesized via ADMET chemistry catalyzed by various catalyst system such as the commercially available Schrock-type molybdenum alkylidene complex, a commercially available Grubbs-type ruthenium carbene (first generation) and a classical

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Scheme 1. Acyclic diene metathesis (ADMET) polymerization.

tungsten-based catalyst [23,24]. Unfortunately, these complexes are difficult to prepare and also so expensive. The aim of the present work is the synthesis of unsaturated ADMET polymers containing organogermanium and organotin units via ADMET in the presence of an alternative catalyst that easier and lower cost in preparation than these catalysts. During past decades, the development of catalyst produced electrochemically has emerged as a mild and efficient means for the formation of carbon–carbon double bonds [25–31]. Electrochemical reduction of WCl_6 and $MoCl_5$ results in the formation of species exhibiting high catalytic activity and stability [25,26]. A recent study reveals the crucial role WCl_5^+ as the only possible active species in the WCl_6-e^- -Al- CH_2Cl_2 system to produce the initial carbene by 1,2-hydride shift following the complexation with the olefin [27]. Continuing research efforts within our group have been devoted some application of WCl_6-e^- -Al- CH_2Cl_2 catalyst system to various olefin metathesis reactions [28–31]. The major advantages of this catalyst system (WCl_6-e^- -Al- CH_2Cl_2) electrochemically generated are low expense of preparation and higher selectivity [25–32]. The WCl_6-e^- -Al- CH_2Cl_2 system easily obtained and is distinguished from the well-known molybdenum and tungsten alkylidenes by being less sensitive to atmospheric oxygen and by retaining its activity for about 10 h [32]. As yet there are relatively few quantitative studies of metathesis reaction of Ge- and Sn-containing dienes. In this paper we report the synthesis of dienes containing the germanium and tin moiety and their polymerization to form unsaturated polycarbogermans and polystannanes using electrochemically produced tungsten-based active species (WCl_6-e^- -Al- CH_2Cl_2).

2. Experimental

2.1. Chemicals

Dialkyldichlorogermane and stannane were purchased from Aldrich and used as received. Akenyl halides were (Aldrich) dried over CaH_2 and distilled immediately before use. WCl_6 was purified by sublimation under nitrogen at about $200^\circ C$ to remove the more volatile WO_2Cl_2 and WCl_4O impurities and kept under nitrogen atmosphere. Dichloromethane (Merck) was washed with concentrated H_2SO_4 , water, an aqueous solution of Na_2CO_3 (5 wt%) and water again. It was dried over anhydrous $CaCl_2$ and then distilled over P_2O_5 under nitrogen. Methanol were supplied from Merck and used as received. THF was distilled from sodium benzophenone kethyl.

2.2. Electrochemical instrumentation

The electrochemical instrumentation consisted of an EGG-PAR Model 273 coupled with a PAR Model Universal Programmer. The measurements were carried out under a nitrogen atmo-

sphere in a three-electrode cell having a jacket through which water from a constant temperature bath was circulated. In the electrochemical experiments, the reference electrode consisted of $AgCl$ coated on a silver wire in $CH_2Cl_2/0.1$ M tetra-*n*-butyl ammonium tetrafluoroborate (TBABF₄), which was separated from the electrolysis solution by a sintered glass disc. Experiments were carried out in an undivided cell with a macro working platinum foil electrode (2.0 cm^2) and aluminium foil (2.0 cm^2) counter electrode.

2.3. Monomer synthesis

2.3.1. Bis(4-pentenyl)di-*n*-butylstannane (**1a**)

A flame-dried round bottom flask was adapted with a reflux condenser and an addition funnel. 0.2 mol magnesium powder was suspended in ca. 80 mL anhydrous diethyl ether. A solution of 0.167 mol 5-bromo-1-pentene in ether (80 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, prior to the slow addition of a solution of 0.049 mol of di-*n*-butyltin dichloride in 50 mL ether. The resulting reaction mixture was refluxed for ca. 24–30 h, cooled to room temperature 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 of pure bis(4-pentenyl)di-*n*-butylstannane, boiling point at 149 – $152^\circ C$. Yield: 78%. 1H NMR: δ (ppm, $CDCl_3$) = 5.7 (m, 2H); 4.89 (m, 4H); 1.99 (q, 4H); 1.48 (m, 4H); 1.38 (m, 4H); 1.24 (m, 4H); 0.82 (m, 14H). ^{13}C NMR δ (ppm, $CDCl_3$) = 138.81 ($CH_2=CH-$), 114.50 ($CH_2=CH-$), 38.26 ($CH_2=CH-CH_2-$), 28.99 ($CH_2=CH-CH_2-CH_2-CH_2-Sn$), 27.42 ($CH_3-CH_2-CH_2-CH_2-Sn$), 26.42 ($CH_3-CH_2-CH_2-CH_2-Sn$), 11.60 ($CH_3-CH_2-CH_2-CH_2-Sn$), 9.89 ($CH_2=CH-CH_2-CH_2-CH_2-Sn$), 8.24 ($CH_3-CH_2-CH_2-CH_2-Sn$).

2.3.2. Bis(4-pentenyl)dimethylstannane

Diene (**1b**) was prepared following the procedure described above. Yield: 72%. 1H NMR: δ (ppm, $CDCl_3$) = 5.82 (ddt, 2H); 5.00 (m, 4H); 2.08 (q, 4H); 1.63 (m, 4H); 0.87 (t, 4H); 0.04 (s, 2H-Sn = 54 Hz, 6H). ^{13}C NMR δ (ppm, $CDCl_3$) = 138.7 ($CH_2=CH-$), 114.4 ($CH_2=CH-$), 38.3 ($CH_2=CH-CH_2-$), 26.3 ($CH_2=CH-CH_2-CH_2-CH_2-Sn$), 9.9 ($CH_2=CH-CH_2-CH_2-CH_2-Sn$), 11.5 (CH_3-Sn).

2.3.3. Bis(4-pentenyl)diphenylstannane

Diene (**1c**) was prepared following the procedure described above. Yield: 69%. 1H NMR: δ (ppm, $CDCl_3$) = 7.48 (d, 4H); 7.18 (m, 6H); 5.66 (m, 2H); 4.94 (m, 4H); 2.02 (q, 4H); 1.66 (m, 4H); 1.22 (t, 4H). ^{13}C NMR δ (ppm, $CDCl_3$) = 142.29 (aromatic,

ipso), 138.38 (CH₂=CH–CH₂–), 137.90 (aromatic, ortho), 128.53 (aromatic, meta, para), 114.87 (CH₂=CH–CH₂–), 38.53 (CH₂=CH–CH₂–), 26.33 (CH₂=CH–CH₂–CH₂–CH₂–Sn), 10.02 (CH₂=CH–CH₂–CH₂–CH₂–Sn).

2.3.4. Bis(4-pentenyl)-diethylgermanium (3a)

A clean, dry three-neck reaction flask equipped with a refluxed condenser, an additional funnel, and a magnetic stir bar was purged with nitrogen and charged with 0.11 mol of freshly ground magnesium turnings and 40 mL of anhydrous THF. 0.08 mol 5-bromo-1-pentene in 30 mL of dry THF was then added to the reaction mixture in small portions via the addition funnel until the reaction began to reflux. The remainder of the solution was then added at a rate that maintained a gentle reflux. The reaction was allowed to stir and refluxed for 0.5 h. The reaction was cooled to room temperature, and 0.024 mol of diethylgermanium dichloride in 30 mL of THF was added dropwise via the addition funnel over a period 1.5 h. Upon completion of the addition, the reaction was stirred for 3 h and then refluxed for 15 h. The reaction was cooled to room temperature, and the solution was poured into 250 mL of ice-cold 1 M aqueous NH₄Cl solution. The organic layer was separated, washed with 300 mL of deionized water, dried over MgSO₄, filtered, and concentrated in vacuo. The remaining liquid was dried over CaH₂ under Schlenk vacuum with collection of the fraction boiling point at 148–152 °C. Yield: 93%. ¹H NMR δ (ppm, CDCl₃) = 5.81 (ddt, 2H); 4.97 (dd, 4H); 2.07 (dt, 4H); 1.45 (m, 4H); 1.03 (t, 6H, CH₃); 0.75 (8H). ¹³C NMR δ (ppm, CDCl₃) = 138.97; 114.41; 37.79; 24.75; 11.46; 9.02; 4.27.

2.3.5. Bis(4-pentenyl)-dimethylgermanium (3b)

Diene **3b** was prepared by a procedure similar to that described above. Yield: 67%. ¹H NMR δ (ppm, CDCl₃) = 5.84 (ddt, 2H); 4.98 (dd, 4H); 2.07 (dt, 4H); 1.49 (m, 4H); 0.74 (m, 4H); 0.07 (s, 6H). ¹³C NMR δ (ppm, CDCl₃) = 138.91; 114.38; 37.46; 24.64; 15.05; –4.21.

2.3.6. Bis(3-butenyl)-diethylgermanium (3c)

Diene **3c** was prepared by a procedure similar to that described above. Yield: 82%. ¹H NMR δ (ppm, CDCl₃) = 5.88; 4.95; 2.15; 1.05; 0.90–0.60. ¹³C NMR δ (ppm, CDCl₃) = 141.64; 112.81; 29.25; 11.14; 8.91; 4.43.

2.4. Activation of catalyst

Electrochemical experiments were performed under a nitrogen atmosphere. WCl₆ (0.2 g, 0.50 mmol) was introduced into the electrochemical cell containing CH₂Cl₂ (25 mL) and a red solution was observed. The electrodes were introduced into the deep red solution and reductive electrolysis at +0.9 V was

applied to the solution for 3 h. The color of the solution darkened progressively. Aliquots from this catalytic solution were used in polymerization reactions.

2.5. Polymerization reactions

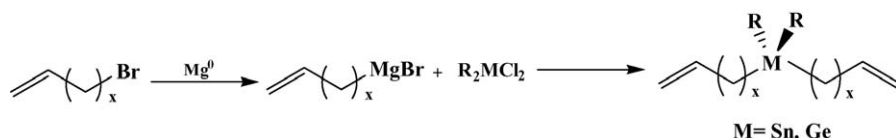
All polymerization reactions were performed using standard Schlenk techniques, at room temperature and under nitrogen atmosphere. A typical polymerization reaction is as follows: monomer (1.6 mmol) was charged to a round bottom flask equipped with a Teflon Roto-flow valve and a magnetic stir bar in a nitrogen-purged dry box. Then 1 mL (0.02 M) of catalytic solution was taken with an automatic pipette from the cell and added to the monomer in a Schlenk tube containing a magnetic stir bar. The valve was sealed and the flask taken from the dry box to a high-vacuum Schlenk line and evacuated while stirring via magnetic agitation. A slow gelation was observed and stirring was continued until ethylene evolution stopped about 24–36 h. Purification of the polymer from dry chloroform into dry methanol using standard Schlenk techniques. The viscous liquid polymers were dried overnight in a vacuum at room temperature. The yields of the polymerizations were determined gravimetrically. The purified polymers were analyzed by ¹H and ¹³C NMR, GPC and DSC techniques.

2.6. Polymer characterization

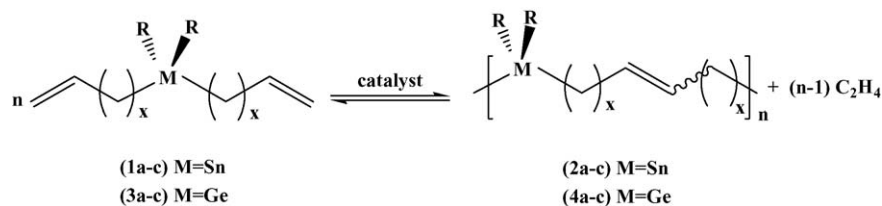
¹H and ¹³C NMR spectra of the obtained polymers were recorded with a Bruker GmbH 400 MHz high-performance digital FT-NMR spectrometer using CDCl₃ as solvent and tetramethylsilane as the reference. Average molecular weight (*M_w*) was determined by gel permeation chromatography. GPC analyses were performed with a Shimadzu LC-10ADVP liquid chromatograph equipped with a Shimadzu SPD-10AVP UV detector, relative to polystyrene standards. Samples were prepared in THF (1%) as eluent and passed through a μ-styragel column. A constant flow rate of 1 mL min^{–1} was maintained at 25 °C. Glass transition temperatures were measured at a heating rate 10 °C/min in the range of –100/+50 °C by Shimadzu DSC-60.

3. Results and discussion

Metal containing unsaturated polymers have various practical applications. Nevertheless, there are only a few polymers made by ADMET polymerization of Ge- and Sn-containing monomers. We have synthesized a series of stannadienes and germadienes by the Grignard alkenylation of dialkyldichlorostannanes and germanes, as illustrated in Scheme 2.



Scheme 2. Synthesis of Sn- and Ge-containing monomers.



Scheme 3. ADMET polymerization of Sn- and Ge-containing monomers.

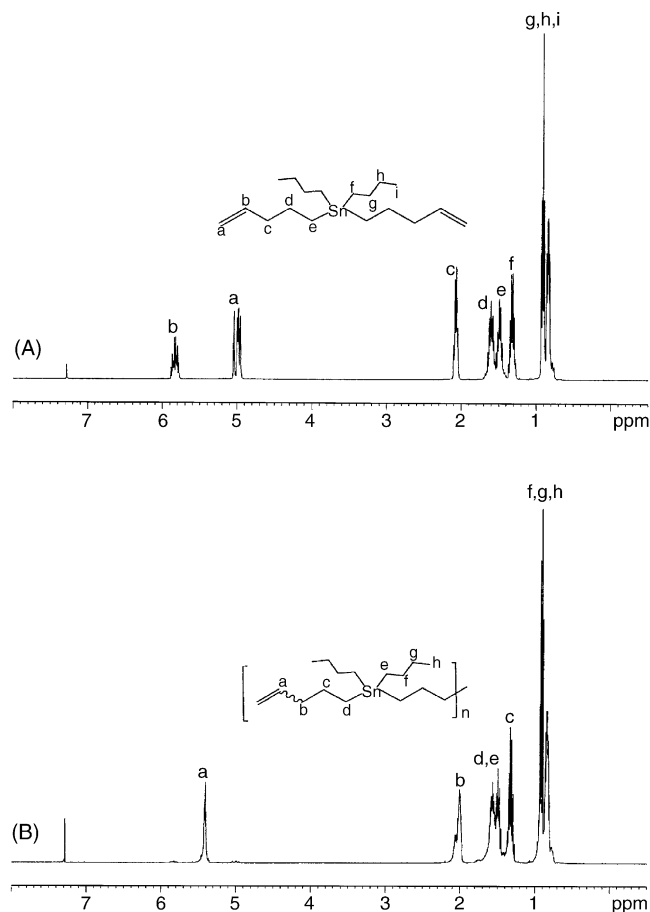
For polymerization study of tin- and germanium-containing monomers, bis(4-pentenyl)di-*n*-butylstannane and bis(4-pentenyl)-diethylgermanium were selected as model monomers on ADMET process. A general polymerization scheme is shown in Scheme 3.

The most important characteristics of ADMET polymerization are the evolution of ethylene and the presence of internal olefin signals in the NMR spectra. Though we did not attempt to detect ethylene, the spectral correlations between the monomer and the polymer showed the loss of terminal olefin groups of the monomer with retention of the internal double bond character in the product. Both the evolution of ethylene and an increase in viscosity is typical of ADMET polymerization. In spite of these similarities, some differences were noted [23,24]. For example, the electrochemically reduced W-based catalyst yielded lower molecular weight polymers than did the alkylidene catalysts. To facilitate the production of higher molecular weight polymers, higher reaction temperature (50 °C) and time (an additional 24 h) were employed. Although there was a decrease in the intensity of signals due to the end groups, there occurred a slight increase in the molecular weight of the polygermanes by using the WCl_6 -e-Al- CH_2Cl_2 catalyst system. However, the electrochemically reduced W-based catalyst appears to have a higher ADMET activity efficiency and selectivity than the alkylidene catalyst, judging by the lower temperature (20–50 °C versus 70 °C) and shorter reaction time (36–48 h versus 72 h) that was employed. All monomer and polymer structures were characterized by 1H and ^{13}C NMR spectroscopy. These results correlate well with the literature [23,24]. For polymerization study of tin- and germanium-containing monomers, bis(4-pentenyl)di-*n*-butylstannane (**1a**) and bis(4-pentenyl)-diethylgermanium (**3a**) were selected models monomer on ADMET process.

The 1H and ^{13}C NMR spectra of the bis(4-pentenyl)di-*n*-butylstannane (**1a**) and its polymer (**2a**) obtained with electrochemically reduced tungsten-based active species are shown in Figs. 1 and 2, respectively. The spectral features of (**2a**) are consistent with the data reported in the literature [23]. A comparison of the NMR spectra of (**1a**) and (**2a**) show the virtual disappearance of the monomer's terminal and appearance of the internal signal, evidence that ADMET polymerization is occurring. In the olefinic region of the ^{13}C NMR spectra of the polymer (**2a**), two peaks can be observed. The peaks at 130.32 and 129.73 ppm correspond to the *trans* and *cis* peaks, respectively. Based on the intensities of these peaks, polymer is assigned to have a higher amount of *trans* configuration. In the non-olefinic region, only one non-olefinic carbon atom which represented by (b) symbol give one peak for each configuration of the double bonds, with C_{bcis} 5.28 ppm upfield from C_{btrans} (at 37.45 ppm). The other

carbon atoms give one peak at 29.28, 27.43, 27.24, 13.76, 8.76 and 8.68 ppm, respectively. The amount of *trans* double which is in accordance with the *cis/trans* ratio found from the ^{13}C NMR olefinic and non-olefinic carbons.

The polymerization of (**3**) gave analogous results with (**1**). The 1H and ^{13}C NMR of bis(4-pentenyl)-diethylgermanium (**3a**) and its polymer (**4a**) are shown in Figs. 3 and 4. These spectra were consistent with literature [24]. Both 1H and ^{13}C NMR of the polymers show the conversion from terminal dienes to internal olefins. New signals at 5.3–5.4 ppm in 1H NMR, and at 129.8–131.6 ppm in ^{13}C NMR account for the new olefin linkages, in both *cis* and *trans* isomeric forms, evidence that metathesis polymerization occurs. The *trans/cis* ratio were established by integration of the corresponding olefinic signals (129 and 132 ppm) and correlated with the intensities of two non-olefinic

Fig. 1. 1H NMR spectra of the (A) bis(4-pentenyl)di-*n*-butylstannane (**1**) and (B) polymer (**1a**).

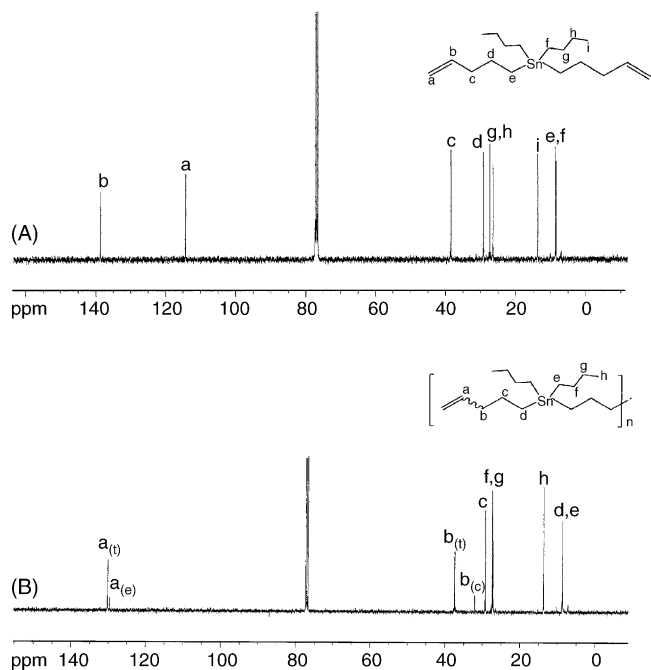


Fig. 2. ¹³C NMR spectra of (A) bis(4-pentenyl)di-*n*-butylstannane (**1**) and (B) polymer (**1a**).

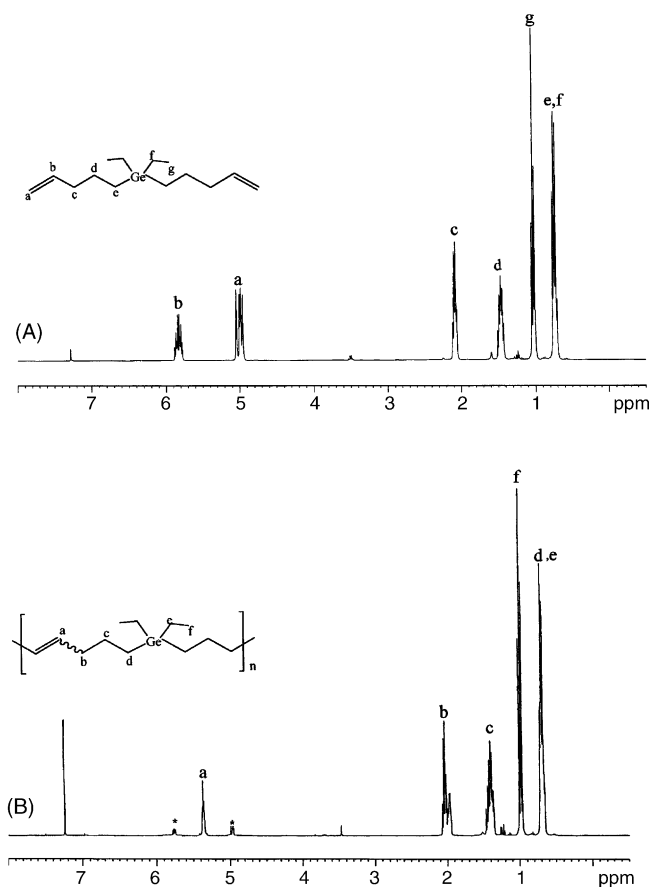


Fig. 3. ¹H NMR spectra of the (A) bis(4-pentenyl)-diethylgermanium (**2**) and (B) polymer (**2a**).

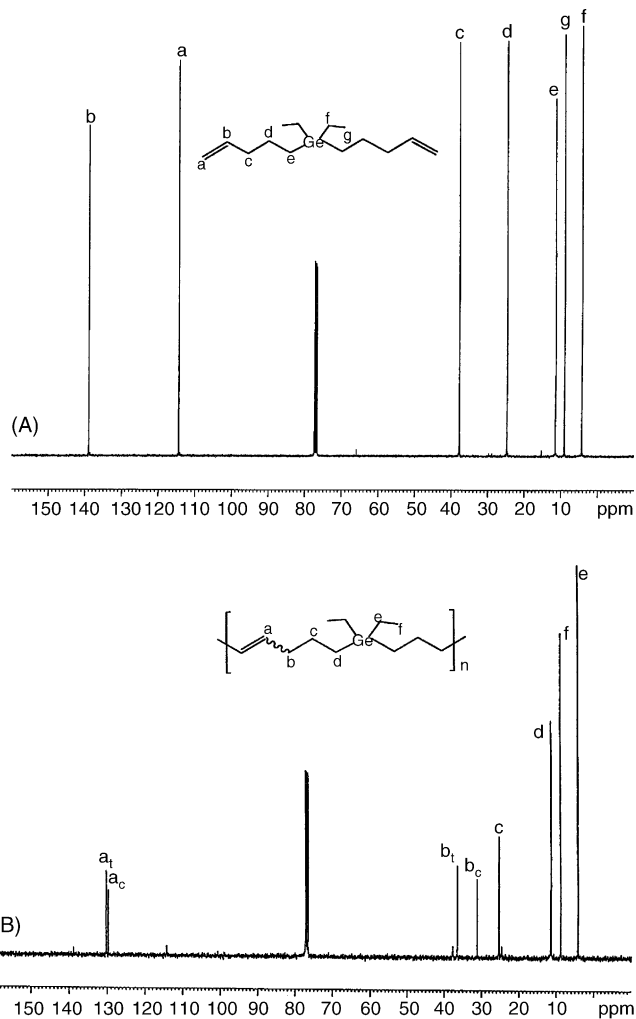


Fig. 4. ¹³C NMR spectra of the (A) bis(4-pentenyl)-diethylgermanium (**2**) and (B) polymer (**2a**).

signals (22/28–31/36 ppm) in the ¹³C NMR. Based on the intensities of these signals, polycarbogermans are assigned to have a higher amount of *trans* configuration. Although the ¹H and ¹³C NMR spectra in the double bond regions are as expected for polygermanes, carbon resonances corresponding to terminal methane and terminal methylene at 5.10 and 5.85 ppm and 114 and 139 ppm, respectively, also exist, indicating that some addition chemistry proceeds as well.

Tables 1 and 2 summarize the polymer characterization data for polycarbostannanes (**2a–c**) and germanes (**4a–c**). The electro-

Table 1
Polymerization data for ADMET polycarbostannanes (**2a–c**)

Polymer	R	<i>n</i>	Yield (%) ^a	<i>Trans</i> (%) ^b	<i>M_w</i> ^c	PDI ^c	<i>T_g</i> ^d (°C)
2a	C ₄ H ₉	3	83	80	35300	2.63	26
2b	CH ₃	3	92	56	32700	2.14	–32
2c	C ₆ H ₅	3	76	67	42500	2.80	–11

^a Determined by gravimetrically.

^b Calculated from ¹³C NMR spectra.

^c Determined by GPC, relative to polystyrene standard.

^d Determined by DSC in N₂ atmosphere.

Table 2
Polymerization data for ADMET polycarbogermanes (**4a–c**)

Polymer	R	n	Yield (%) ^a	Trans (%) ^b	M _w ^c	PDI ^c	T _g ^d (°C)
4a	C ₂ H ₅	3	87	57	19100	2.17	–24
4b	CH ₃	3	68	63	7400	2.34	–9
4c	C ₂ H ₅	2	85	70	17700	1.98	–47

^a Determined by gravimetrically.

^b Calculated from ¹³C NMR spectra.

^c Determined by GPC, relative to polystyrene standard.

^d Determined by DSC in N₂ atmosphere.

chemical tungsten-based system leads to a mainly *trans* product (ca. 56–80% *trans*) in the production of polycarbostannanes and polycarbogermanes, which exhibit similar stereochemical characteristics to those seen in the other ADMET systems [23,24]. Polymer exhibit only one transition between –100 and +50 °C. This transition is the glass transition temperature with no detectable melting transition. This DSC result reveals that the polymer is completely amorphous.

Average molecular weight (*M_w*) was determined by gel permeation chromatography displayed that the polydispersity of the polymers approximately two exists, as is expected for equilibrium step propagation, condensation type polymerization. Molecular weights of this order of magnitude are relatively lower than expected by ADMET-type polymerizations. A factor might be the accompanying vinyl addition reactions leading to the formation of cross-linked, insoluble polymer as a side product.

4. Conclusion

Polymers containing tin and germanium have been efficiently synthesized via ADMET in the presence of electrochemically produced tungsten-based active species (WCl₆-e⁻-Al-CH₂Cl₂). The major advantages of this catalyst system electrochemically generated are low expense of preparation and higher selectivity. In addition, this catalyst system easily obtained and is distinguished from the well-known molybdenum and tungsten alkylidenes by being less sensitive to atmospheric oxygen and by retaining its activity for about 10 h. The electrochemically generated tungsten-based catalyst seem to be more active than the other catalyst systems in the ADMET polymerization of tin and germanium-containing monomers due to higher polymerization yields and shorter reaction periods. The electrochemical tungsten-based system leads to polymers of lower molecular weight and higher polydispersity in comparison with the other ADMET systems. The WCl₆-e⁻-Al-CH₂Cl₂ catalyst system produced various unsaturated polymers containing the germanium and tin with high *trans* content, exhibiting similar stereochemical characteristics seen in the previous ADMET systems.

Acknowledgements

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