

Electronic Supplementary Information for

## **Addition Polymerization of 1,1-Dimesitylneopentylgermene: Synthesis of a Polygermene**

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### **Experimental Procedures:**

#### General Experimental Details.

All reactions were carried out under an inert atmosphere (argon) in flame-dried glassware. The C<sub>6</sub>D<sub>6</sub> was distilled from LiAlH<sub>4</sub>, stored over 4 Å molecular sieves, and degassed prior to use. Pentane was dried using a solvent purification system (Innovative Technologies Inc., Newburyport, Massachusetts) in which the solvent was passed through an alumina-packed column. Dichloromethane and methanol were purchased from Caledon Laboratories Ltd. *t*-Butyllithium (1.7 M) was purchased from the Aldrich Chemical Co. and used without purification. 1,1-Dimesitylneopentylgermene (**1**) and fluorovinylgermane **2** were prepared according to reported procedures.<sup>1</sup>

The NMR spectra were recorded on a Varian Inova 400 or Inova 600 spectrometer. The internal NMR standards used were residual C<sub>6</sub>D<sub>5</sub>H (7.15 ppm) or CHCl<sub>3</sub> (7.25 ppm) for <sup>1</sup>H NMR spectra and the central signal of C<sub>6</sub>D<sub>6</sub> (128.0 ppm) or CDCl<sub>3</sub> (77.0 ppm) for <sup>13</sup>C NMR spectra. Thermal gravimetric analysis was performed on a Mettler Toledo TGA/SDTA851<sup>e</sup> instrument with a heating rate of 10 °C/min.

Differential scanning calorimetry was performed on a Mettler Toledo DSC822° instrument with a heating rate of 10 °C/min. The IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. Electron impact mass spectra were obtained using a MAT model 8400 mass spectrometer. Mass spectral data are reported in mass-to-charge ratios ( $m/z$ ).

The molecular weight of polymer **3** (synthesized from **2**) was estimated relative to polystyrene standards by size-exclusion chromatography (SEC) using equipment supplied by Polymer Laboratories Ltd. All determinations were carried out at 40°C using a GPC system consisting of a Polymer Lab LC 1120 HPLC pump, a Polymer Labs Shodex Refractive Index detector, a Knauer K-2600 variable dual wavelength UV-vis detector and two 300 mm x 7.5 mm PLGel 5 µm mixed-C columns. THF (HPLC grade) was used as an eluent and was set to a flow rate of 1ml min<sup>-1</sup>. All GPC measurements were interpreted using the Cirrus GPC online computer software version 2.0.

Molecular weights of the remaining polymers were also estimated relative to polystyrene standards by size-exclusion chromatography at 40 °C. The GPC system consisted of a Waters 515 HPLC pump, a Wyatt Optilab rEX Refractive Index detector, a Wyatt miniDAWN TREOS triple-angle light scattering detector, and two 300 mm x 7.5 mm Resipore columns from Polymer Laboratories. THF (HPLC grade) was used as an eluent and was set to a flow rate of 0.75 ml min<sup>-1</sup>. All GPC measurements were interpreted using the Astra online computer software version 5.3.2.

Synthesis of **3** from **1**.

*t*-Butyllithium (1.7 M, 0.05 mL, 0.08 mmol) was added to a pale yellow solution of **1** (200 mg, 0.51 mmol) in pentane (6 mL) at room temperature. The colour of the solution changed from pale to bright yellow. After the solution was allowed to stir for 30 min, methanol (1 drop) was added and the bright yellow colour of the solution dissipated immediately. The solvents were removed under vacuum and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). A white solid precipitated upon slow addition of methanol (10 mL) to the CH<sub>2</sub>Cl<sub>2</sub> solution. The solid was purified by reprecipitation. The air stable material was isolated in 45% yield.

**3**: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.6 (br, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 0.8 – 1.5 (br, 3 H, GeCH<sub>2</sub>, GeCHCH<sub>2</sub>), 1.6 – 3.1 (br, 18 H, *o/p*-Mes CH<sub>3</sub>), 6.5 (br, 4 H, Mes-H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 16.7 (br, GeCH), 20.6 (*p*-Mes CH<sub>3</sub>), 20.9 (*p*-Mes CH<sub>3</sub>), 24.3 (br, *o*-Mes CH<sub>3</sub>), 28.9 (C(CH<sub>3</sub>)<sub>3</sub>), 31.1 (C(CH<sub>3</sub>)<sub>3</sub>), 38.7 (br, GeCHCH<sub>2</sub>), 128.5 (br, *m*-Mes C), 129.2 (br, *m*-Mes C), 136.2 (br, *p*-Mes C), 136.8 (br, *p*-Mes C), 140.0 (br, *i*-Mes C), 142.6 (br, *o*-Mes C), 144.8 (br, *o*-Mes C); GPC (THF, vs. polystyrene) *M*<sub>n</sub> = 36 000 gmol<sup>-1</sup>, PDI = 1.5; *M*<sub>n</sub> = 7 100 gmol<sup>-1</sup>, PDI = 1.1.

#### Synthesis of **3** from **2**.

*t*-Butyllithium (1.7 M, 0.36 mL, 0.61 mmol) was added to a solution of **2** (200 mg, 0.56 mmol) in pentane (6 mL), cooled by a Dry Ice/acetone bath. The solution was allowed to warm to room temperature and then was stirred for 30 min. The colour of the solution changed from pale to bright yellow at room temperature. Methanol (1 drop) was added to the reaction mixture, at which point the colour dissipated. The pentane solution was washed with water, dried over MgSO<sub>4</sub>, and filtered. The solvent was removed on a rotary

evaporator. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and a white solid precipitated upon dropwise addition of methanol (10 mL). The polymer was isolated in 62% yield. GPC (THF, vs. polystyrene)  $M_n = 39\ 000\ \text{g mol}^{-1}$ , PDI = 2.0.

#### Synthesis of **4a,b** and **5**

A solution of **2** (200 mg, 0.56 mmol) in pentane (6 mL) was cooled in Dry Ice/acetone. *t*-Butyllithium (1.7 M, 0.3 mL, 0.51 mmol) was added to the solution, which was then allowed to warm to room temperature. The pentane was removed under vacuum and the residue was dissolved in C<sub>6</sub>D<sub>6</sub> (3 mL). The progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy. After 10 days, germene **1** was consumed. The C<sub>6</sub>D<sub>6</sub> was removed under vacuum and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The polymeric material was precipitated with methanol (25 wt%); GPC (THF, vs. polystyrene)  $M_n = 21\ 000\ \text{g mol}^{-1}$ , PDI = 2.5). The cyclic dimers (**4a,b**) and germane **5** remained in the mother liquor. Minor amounts of (*t*-BuCH<sub>2</sub>CH<sub>2</sub>Mes<sub>2</sub>Ge)<sub>2</sub>O<sup>1</sup> were also observed. The *trans* dimer (**4a**) was isolated from the mixture after crystallization from a concentrated C<sub>6</sub>D<sub>6</sub> solution; attempts to separate the *cis* dimer (**4b**) from germane **5** and the digermoxane by chromatography were unsuccessful.

**4a**: mp 280 °C (decomp.); IR (cm<sup>-1</sup>) 2950, 2867, 1605, 1560, 1450, 1408, 1368, 1036, 849; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 0.80 (s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.71 (d, *J* = 5.4 Hz, 4 H, GeCHCH<sub>2</sub>), 2.12 (s, 12 H, *p*-Mes CH<sub>3</sub>), 2.47 (br, 24 H, *o*-Mes CH<sub>3</sub>), 3.63 (t, *J* = 5.4 Hz, 2 H, GeCH), 6.76 (s, 8 H, Mes-H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 20.94 (*p*-Mes CH<sub>3</sub>), 26.23 (*o*-Mes CH<sub>3</sub>), 29.88 (C(CH<sub>3</sub>)<sub>3</sub>), 32.04 (C(CH<sub>3</sub>)<sub>3</sub>), 37.66 (Ge-CH), 41.73 (Ge-CHCH<sub>2</sub>), 129.39 (*m*-Mes C),

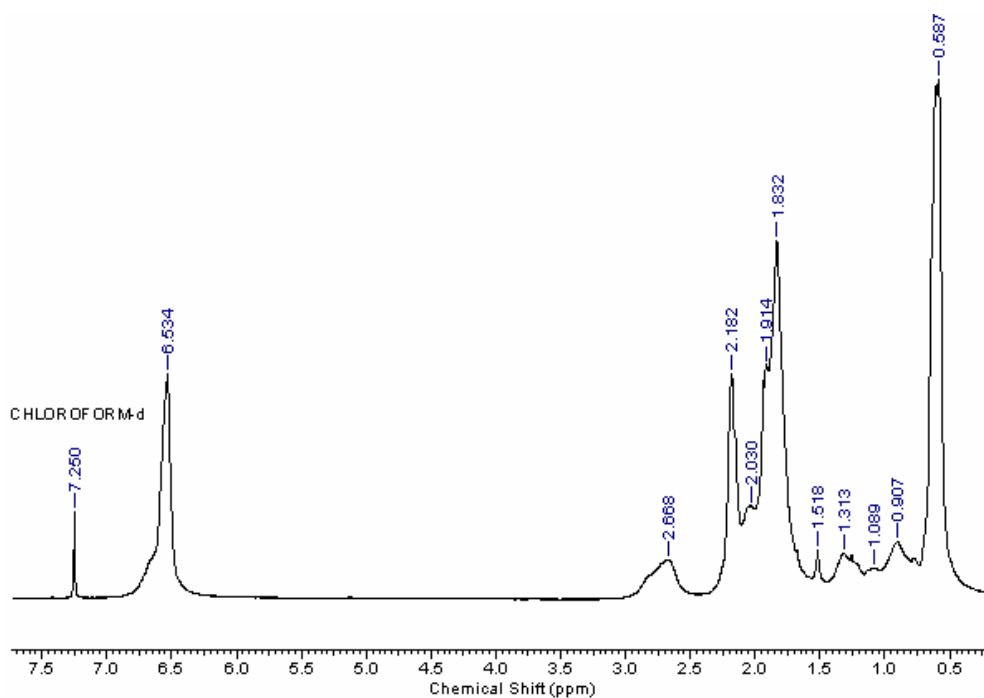
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137.61 (*i*-Mes C), 138.00 (*p*-Mes C), 143.45 (*o*-Mes C); High-resolution EI-MS for  $^{70}\text{Ge}^{72}\text{GeC}_{48}\text{H}_{68}$   $m/z$  calcd 786.3784, found 786.3801.

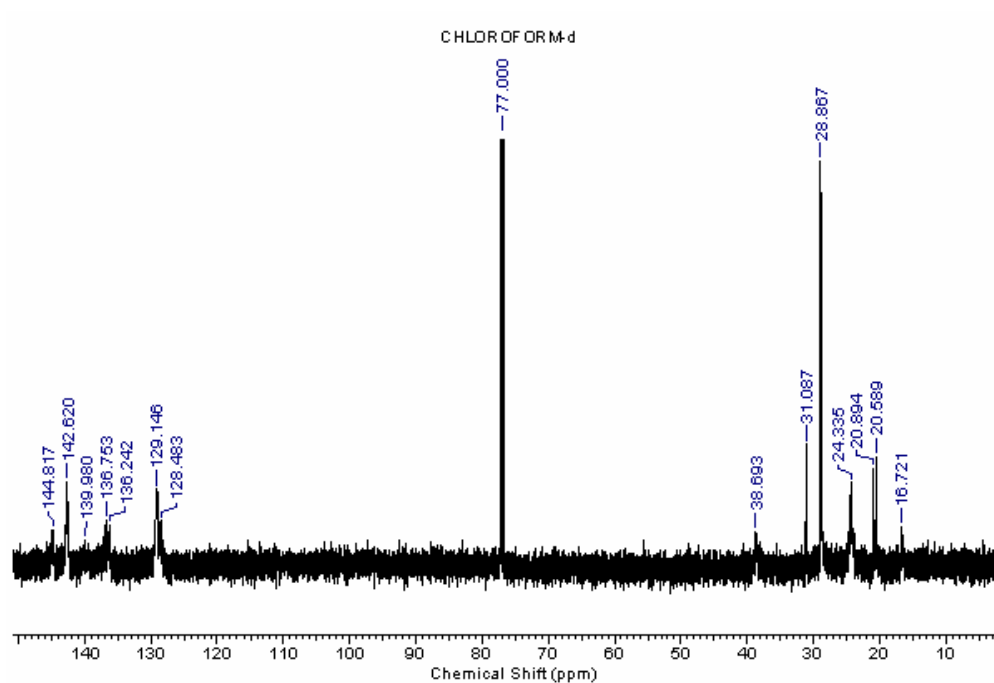
**4b**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.87 (s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>), 2.09 (s, 6 H, *p*-Mes CH<sub>3</sub>), 2.14 (s, 6 H, *p*-Mes CH<sub>3</sub>), 2.28 (br, 12 H, *o*-Mes CH<sub>3</sub>), 2.31 (d,  $J = 6$  Hz, 4 H, GeCHCH<sub>2</sub>), 2.49 (br, 12 H, *o*-Mes CH<sub>3</sub>), 3.06 (t,  $J = 6$  Hz, 2 H, GeCH), 6.74 (s, 4 H, Mes-H), 6.77 (s, 4 H, Mes-H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  20.91 (*p*-Mes CH<sub>3</sub>), 20.95 (*p*-Mes CH<sub>3</sub>), 25.02 (*o*-Mes CH<sub>3</sub>), 26.23 (*o*-Mes CH<sub>3</sub>), 29.85 (C(CH<sub>3</sub>)<sub>3</sub>), 32.34 (C(CH<sub>3</sub>)<sub>3</sub>), 36.48 (Ge-CH), 43.89 (Ge-CHCH<sub>2</sub>), 129.11 (*m*-Mes C), 129.85 (*m*-Mes C), 137.61 (*p*-Mes C), 138.11 (*p*-Mes C), 138.83 (*i*-Mes C), 142.18 (*i*-Mes C), 142.38 (*o*-Mes C), 143.20 (*o*-Mes C); EI-MS for  $^{74}\text{Ge}_2\text{C}_{48}\text{H}_{68}$   $m/z$  790.5 ( $\text{M}^+$ , 1.1), 622.2 ( $^{74}\text{Ge}_2\text{Mes}_4$ , 31).

**5**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.93 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 2.11 (s, 6 H, *p*-Mes CH<sub>3</sub>), 2.41 (s, 12 H, *o*-Mes CH<sub>3</sub>), 5.84 (d,  $J = 2.4$  Hz, 1 H, Ge-H), 6.17 (AB,  $J = 18$  Hz, 1 H, Ge-CH=CH), 6.20 (d of AB,  $J = 18$  Hz, 3.0 Hz, Ge-CH=CH), 6.75 (s, 4 H, Mes-H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  21.02 (*p*-Mes CH<sub>3</sub>), 24.00 (*o*-Mes CH<sub>3</sub>), 28.91 (C(CH<sub>3</sub>)<sub>3</sub>), 35.12 (C(CH<sub>3</sub>)<sub>3</sub>), 121.51 (Ge-CH=CH), 129.16 (*m*-Mes C), 133.72 (*i*-Mes C), 138.39 (*p*-Mes C), 143.63 (*o*-Mes C), 156.38 (Ge-CH=CH); High-resolution EI-MS for  $^{70}\text{GeC}_{24}\text{H}_{34}$   $m/z$  calcd 392.1903, found 392.1899.

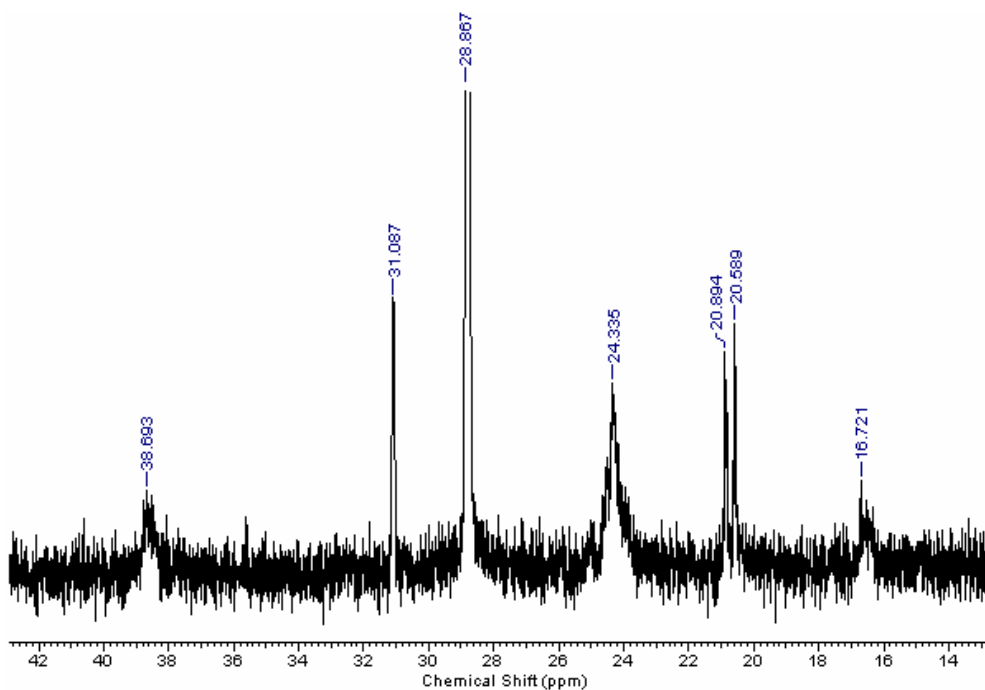
**Fig. S1**  $^1\text{H}$  NMR spectrum of **3** in  $\text{CDCl}_3$  at 25 °C.



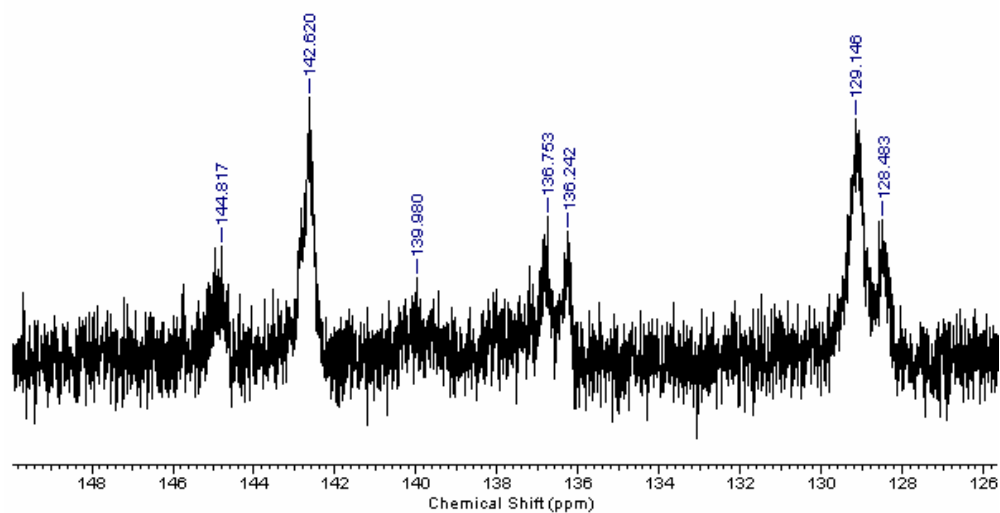
**Fig. S2**  $^{13}\text{C}$  NMR spectrum of **3** in  $\text{CDCl}_3$  at 25 °C.



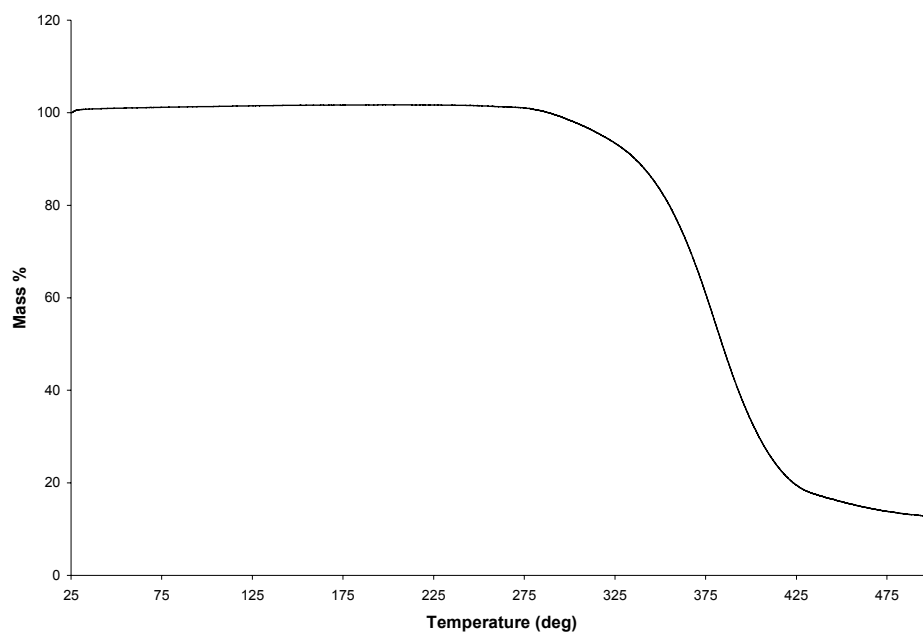
**Fig. S3** Expansion (aliphatic region) of  $^{13}\text{C}$  NMR spectrum of **3** in  $\text{CDCl}_3$  at 25 °C.



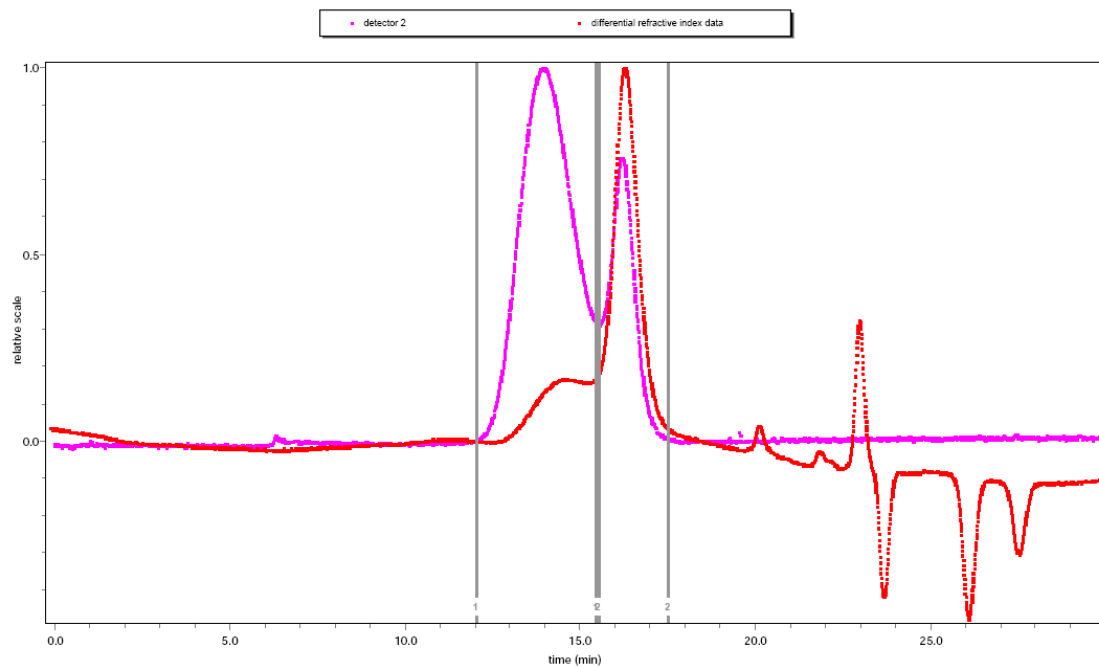
**Fig. S4** Expansion (aromatic region) of  $^{13}\text{C}$  NMR spectrum of **3** in  $\text{CDCl}_3$  at 25 °C.



**Fig. S5** TGA scan of **3**.

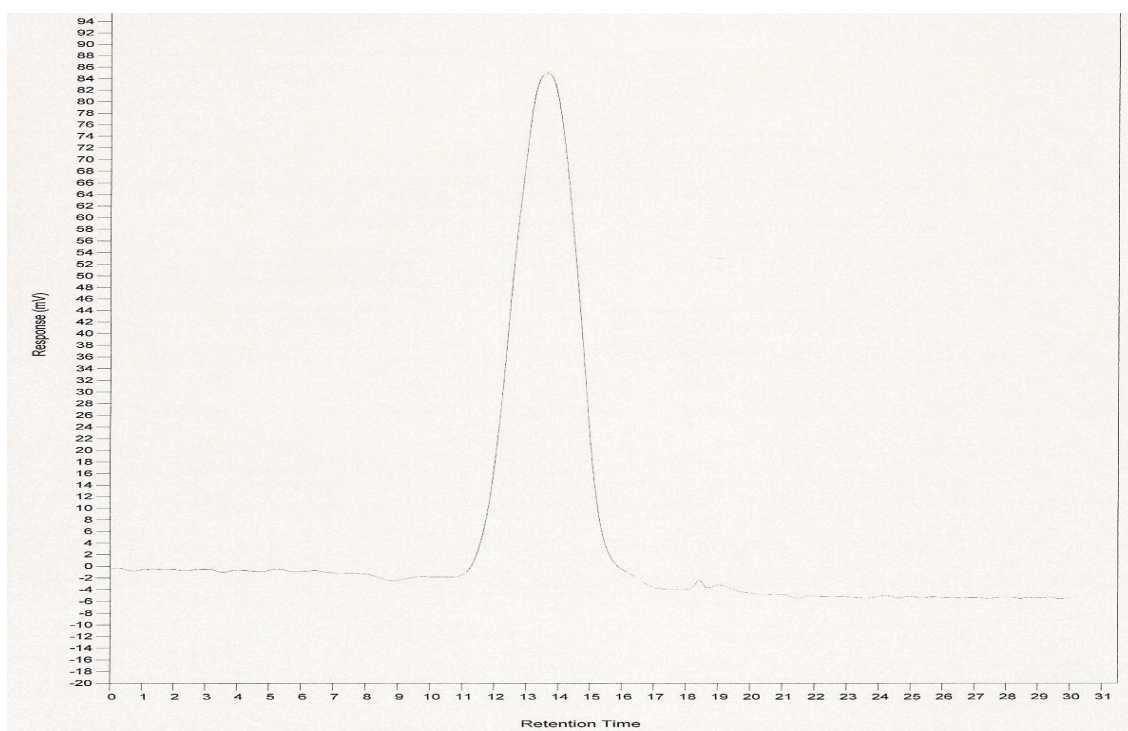


**Fig. S6** GPC trace of **3** (synthesized from **1**).

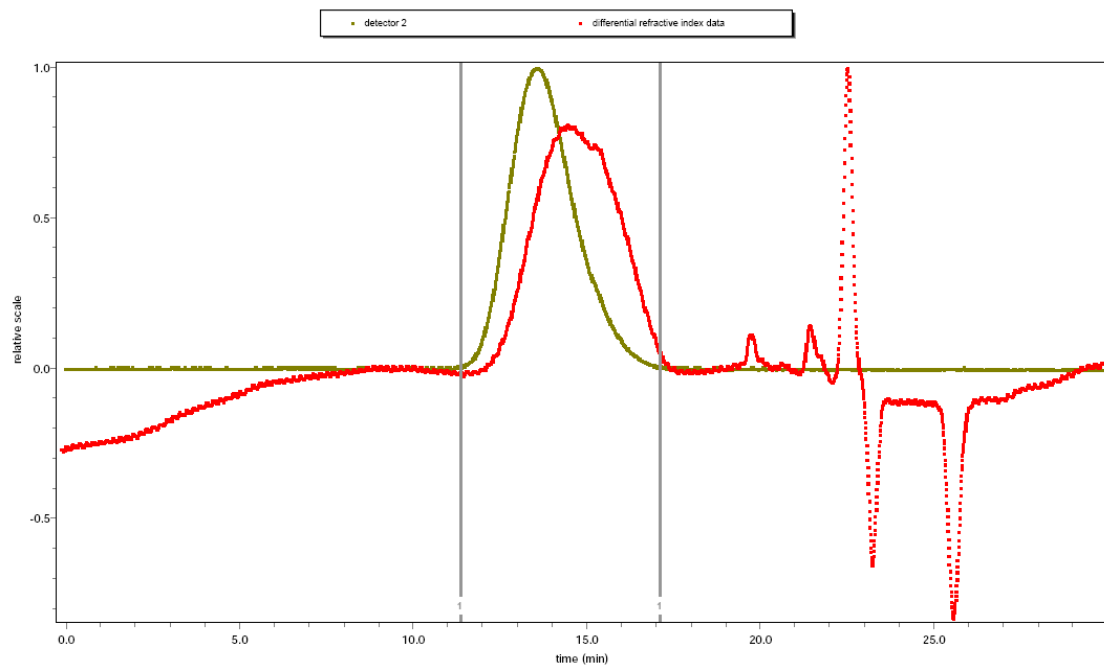




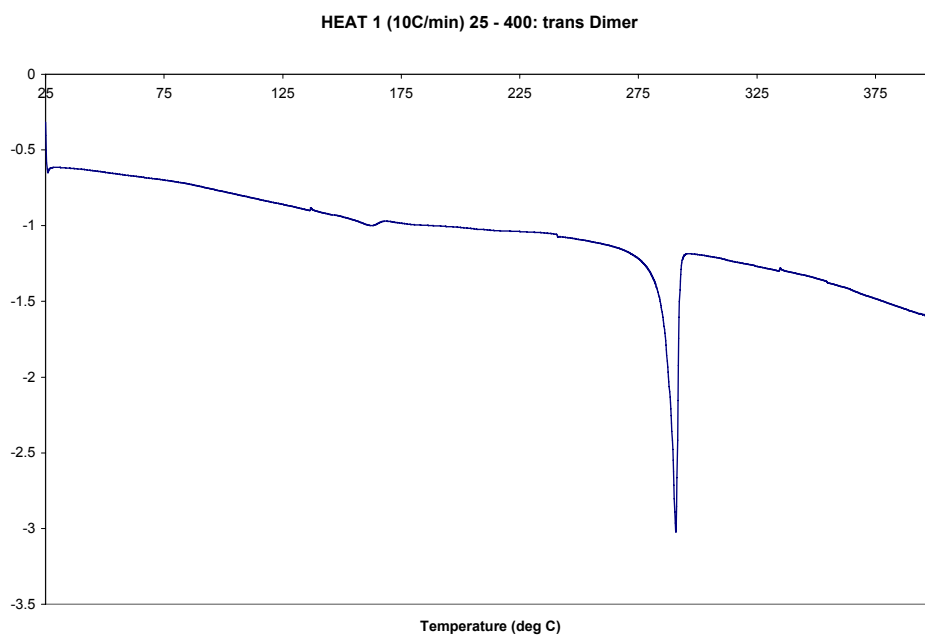
**Fig. S7** GPC trace of **3** (synthesized from **2**).



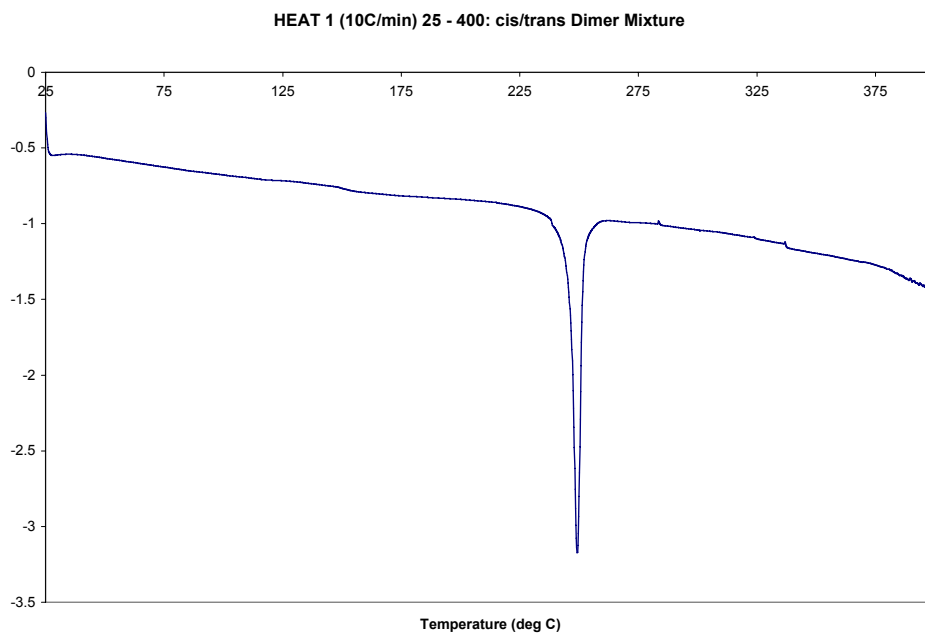
**Fig. S8** GPC trace of **3** (no initiator).



**Fig. S9** DSC trace of **4a** (25 – 400 °C; 10 °C/min).



**Fig. S10** DSC trace of **4a/b** mixture (25 – 400 °C; 10 °C/min).



**X-Ray Structure of 4a:**

Crystals of **4a** were grown by slow evaporation of a concentrated C<sub>6</sub>D<sub>6</sub> solution containing **4a**, **4b**, and **5**. A colourless crystal was mounted on a glass fibre. Data were collected at low temperature (150(2) K) on a Nonius Kappa-CCD area detector diffractometer with COLLECT (Nonius B.V., 1997-2002). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN.<sup>2</sup> The absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK). The crystal data and refinement parameters are listed in Table S1. The reflection data and systematic absences were consistent with a triclinic space group: P  $\bar{1}$ .

The SHELXTL/PC V6.14 for Windows NT (Sheldrick, G. M., 2001) suite of programs was used to solve the structure by direct methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located. There were two nearly identical half molecules in the asymmetric unit each lying about a centre of inversion. As a result, the symmetry generated digermacyclobutane rings are exactly planar. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms.

Full-matrix least squares refinement of F<sup>2</sup> gave R<sub>1</sub> = 3.98 for 2σ data and wR<sub>2</sub> = 10.16 for all data (GOOF = 1.047). The final solution was submitted to the IUCR checkCIF program and had no Alert Levels A or B.

**Table S1.** X-Ray Crystallographic Data for **4a**

Formula	C <sub>48</sub> H <sub>68</sub> Ge <sub>2</sub>
Fw	790.20
Wavelength	0.71073
<i>T</i> (K)	150(2)
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	12.5026(4)
<i>b</i> (Å)	13.2978(4)
<i>c</i> (Å)	14.0760(4)
$\alpha$ (deg)	102.1924(16)
$\beta$ (deg)	104.8630(15)
$\gamma$ (deg)	92.3110(14)
<i>V</i> (Å <sup>3</sup> )	2199.83(12)
<i>Z</i>	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.193
Absorption coefficient (mm <sup>-1</sup> )	1.396
<i>F</i> (000)	840
Crystal size (mm <sup>3</sup> )	0.38 x 0.23 x 0.18
$\theta$ range for data collection (deg)	2.04 to 27.48
Reflections collected	17043
Independent reflections	10107; R(int) = 0.037
Completeness (%)	99.5
Absorption correction	Semi-empirical from equivalents
Data/restraints/parameters	10107/0/469
Goodness-of-fit <i>F</i> <sup>2</sup>	1.047
Final R indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )	R <sub>1</sub> = 0.0398; wR <sub>2</sub> = 0.0909
R indices (all data)	R <sub>1</sub> = 0.0691; wR <sub>2</sub> = 0.1016
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.444; -0.565

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**References:**

- 1 C. Couret, J. Escudié, G. Delpon-Lacaze and J. Satgé, *Organometallics*, 1992, **11**, 3176.
- 2 Z. Otwinowski and W. Minor in *Methods in Enzymology, Vol. 276: Macromolecular Crystallography, Part A*. Edited by C. W. Carter Jr. and R. M. Sweet; Academic Press: New York, 1997; p. 307.