



Synthesis of 1,1-bis(silyl)-1-alkene derivatives bearing Si–H functional groups via Peterson protocol

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ABSTRACT

Various aromatic aldehydes were converted to one-carbon elongate 1,1-bis(silyl)-1-alkene derivatives bearing Si–H functional and reactive groups in a convenient one-pot operation via the Peterson protocol. Then poly(styrene) and poly(α -methylstyrene) (**I&II**) random homopolymers were synthesized by solution free radical polymerization at $70(\pm 1)$ °C using α,α' -azobis(isobutyronitrile) (AIBN) as an initiator. The aldehyde group is introduced by direct electrophilic substitution of polymers **I** and **II**. This formylation reaction was conducted in two different solvents: dichloromethane (CH_2Cl_2) and nitrobenzene (PhNO_2). The results indicate that PhNO_2 appeared to be a more suitable solvent for such an aldehyde functionalization of the polymers. The formylated polymers (**I**_{CHO}, **II**_{CHO}) were then converted to Si–H functionalized polymers (**I**_{Si–H}, **II**_{Si–H}) via reaction with tris(dimethylsilyl)methyl lithium, $(\text{HMe}_2\text{Si})_3\text{CLi}$.

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1. Introduction

1,1-Dimetalated-1-alkenes constitute an important class of organometallic reagents which are currently widely used as potential intermediates in the organic and organometallic synthesis. Among the most notable and commonly employed gem-diorganometallics, the 1,1-bis(silyl)-1-alkenes are of unique importance. Their use as precursors for the preparation of ketones as well as variety of important organosilicon intermediate such as acylsilanes, epoxysilanes, 1-halovinylsilanes, silylenoethers, (*E*)-alkenylsilanes, silylenolacetates etc., stimulate interest in their synthetic availability [1–8].

Introduction of functional groups on a polymer chain results in modification of many properties of polymer such as thermal and mechanical properties, gas permeabilities, polarity, solubility, adhesion, etc. For example, it is known that the polymers containing tris(trimethylsilyl)methyl, $(\text{Me}_3\text{Si})_3\text{C}-$, group have excellent permeability. Therefore, the preparation of macromolecules containing the organosilyl groups and studying their properties are a novel field in polymer and silicon chemistry [9–13].

By using the Peterson olefination reaction, synthetically useful vinylsilanes can be prepared by the reaction of bis(silyl)methyl metal with carbonyl compounds using the direct addition–elimination process [14–16]. Despite many useful studies of Peterson olefination reaction over the conventional carbonyl olefination

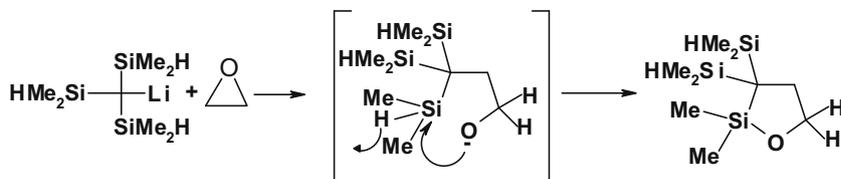
reaction, there are a few reports about the preparation of 1,1-bis(silyl)-1-alkenes in the literature from this protocol [17]. However, as far as we are aware, there has hitherto been no references in the literature about the preparation of 1,1-bis(silyl)-1-alkenes containing Si–H functional and reactive group by this method. Herein, we employed the Peterson protocol to synthesize 1,1-bis(silyl)-1-alkenes bearing Si–H groups. Moreover, we carried out the same reaction on the side chain of formylated styrene polymers to synthesize functionally new macromolecules containing Si–H groups.

2. Results and discussion

Recently, we have embarked on a program directed towards the development of tris(dimethylsilyl)methyl lithium, $(\text{HMe}_2\text{Si})_3\text{CLi}$, reaction for the generation of synthetically useful organosilicon compounds [18,19]. We paid particular attention to epoxides because of their ring opening reaction and the potentially coordination of the produced alkoxide group to silicon, thereby enabling the facile cyclization. For example, when $(\text{HMe}_2\text{Si})_3\text{CLi}$ reacts with ethylene oxide in THF at -5 °C, it seems that because of the existence of the Si–H bond, an intramolecular alkoxylation takes place and the cyclic product forms (Scheme 1) [18]. In ongoing effort to exploit $(\text{HMe}_2\text{Si})_3\text{CLi}$, we envisioned that appending $(\text{HMe}_2\text{Si})_3\text{CLi}$ ligand to carbonyl group should lead to interesting compounds.

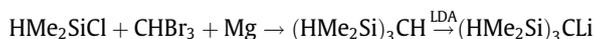
The starting point of the work was the compound tris(dimethylsilyl)methane, $(\text{HMe}_2\text{Si})_3\text{CH}$, which was made in 60% yield from HMe_2SiCl , CHBr_3 and Mg in THF. $(\text{HMe}_2\text{Si})_3\text{CH}$ was then metallated

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Scheme 1. Preparation of silacyclopentane via the reaction of $(\text{HMe}_2\text{Si})_3\text{CLi}$ with ethylene oxide.

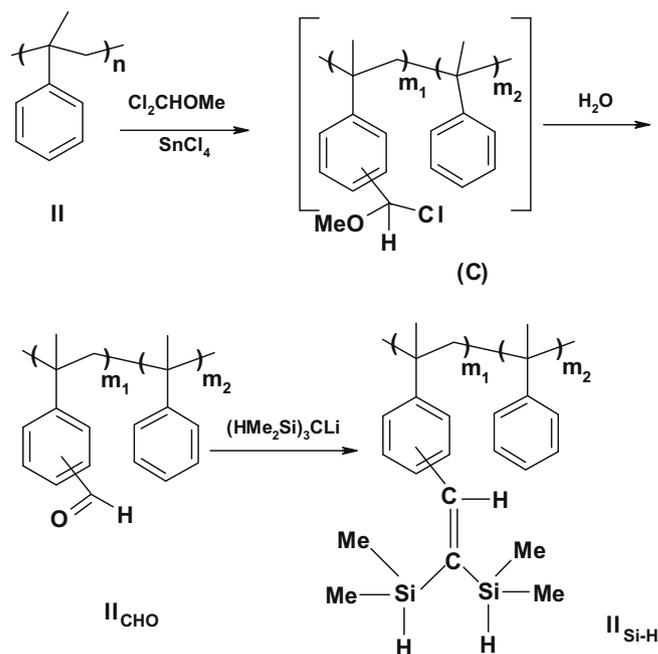
with lithiumdiisopropylamide (LDA) during 6 h and gave $(\text{HMe}_2\text{Si})_3\text{CLi}$ [20].



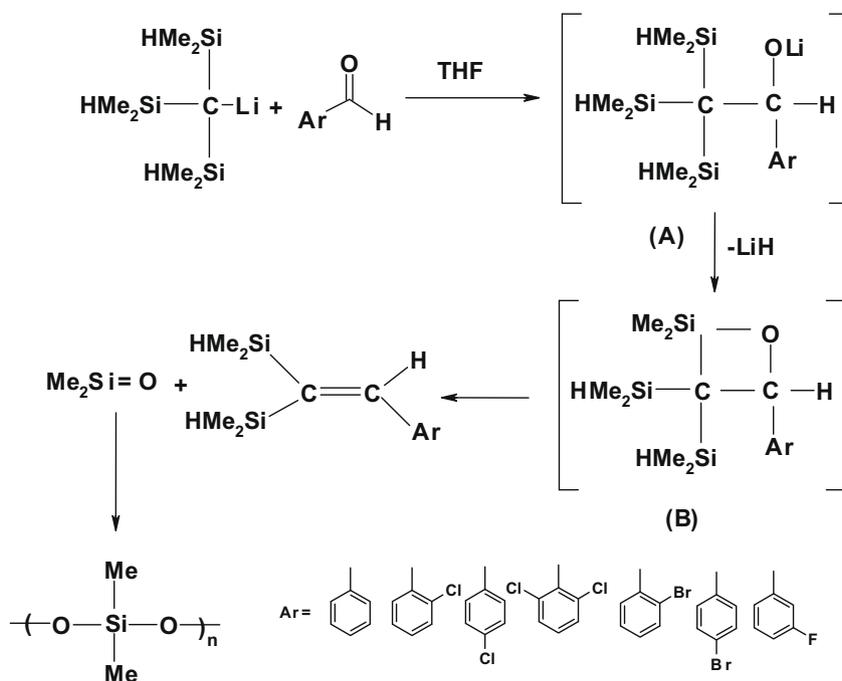
$(\text{HMe}_2\text{Si})_3\text{CLi}$ reacts with non-enolisable aldehydes such as benzaldehyde, *o*-chloro, *p*-chloro, 2,6-dichloro, *o*-bromo, *p*-bromo, and *m*-fluoro benzaldehyde with the formation of carbon–carbon double bond. This method of preparing functionalized silanes is limited by the readiness with which $(\text{HMe}_2\text{Si})_3\text{CLi}$ abstracts a proton, if one is available, rather than attacking the carbonyl group. The Peterson reactions readily take place and give the corresponding 1,1-bis(silyl)-1-alkene derivatives.

We postulated that when $(\text{HMe}_2\text{Si})_3\text{CLi}$ is treated with carbonyl group, it initially forms the alkoxide intermediate (A), then because of the presence of the Si–H bond, an intramolecular alkoxide attack takes place and gives (B). It seems likely that the cyclic intermediate (B) is unstable and swiftly converts to 1,1-bis(silyl)-1-alkene with the elimination of Me_2SiO (Scheme 2).

We were also interested in carrying out analogous reactions with polymers containing carbonyl groups in the side chains. For this reason poly(styrene) and poly(α -methylstyrene) (I, II) were formylated by methyl dichloromethyl ether (Cl_2CHOMe) in the presence of tin (IV) chloride (SnCl_4) [21]. We found that solvent plays an important role in the completion of the formylation reaction. When CH_2Cl_2 is employed as a solvent, the ^1H NMR spectrum shows two signals for OMe and CHCl which indicates that the hydrolysis step of the intermediate (C) is not complete, probably due to insolubility of the resulted polymer in CH_2Cl_2 (Scheme 3).



Scheme 3. Preparation of formylated polymer II_{CHO} and its conversion to functional polymer $\text{II}_{\text{Si-H}}$.



Scheme 2. Treatment of some non-enolisable aldehydes with $(\text{HMe}_2\text{Si})_3\text{CLi}$.

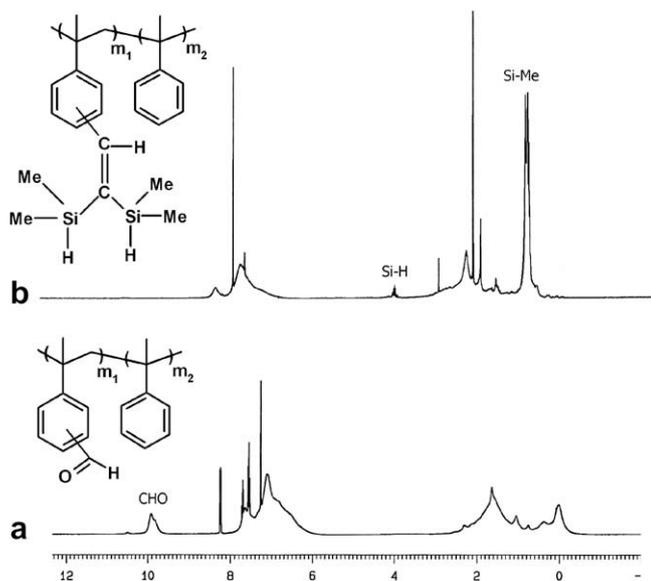


Fig. 1. The ^1H NMR spectra of (a) II_{CHO} and (b) $\text{II}_{\text{Si-H}}$.

In contrast, using PhNO_2 as a solvent eliminates the mentioned signals in ^1H NMR which clearly demonstrates that the hydrolysis of the intermediate (C) was completed in this solvent.

The percentage of formyl in polymer II_{CHO} side chain was calculated by measuring the integrated peak areas of the formyl proton and total aliphatic protons. The expression in Eq. (1) was used to determine the composition of the polymer, where m_1 is the mole fraction of formyl α -methylstyrene and $1 - m_1$ is that of α -methylstyrene. Both formyl α -methylstyrene and α -methylstyrene contain 5 aliphatic protons. Based on the mentioned calculation, incorporation of formyl in the side chain of polymer I_{CHO} and II_{CHO} were assigned 49 and 52 mol%, respectively

$$\frac{I_A}{I_a} = \frac{\text{integrated peak area of formyl protons}}{\text{integrated peak area of aliphatic protons}}$$

$$\frac{I_A}{I_a} = \frac{m_1}{5m_1 + 5(1 - m_1)}$$

on simplification, This gives

$$m_1\% = \frac{5I_A}{I_a} \times 100 \quad (1)$$

The new copolymers containing bis(silyl)alkenes ($\text{I}_{\text{Si-H}}$ and $\text{II}_{\text{Si-H}}$) were synthesized by the treatment of carbonyl group in the side chain of copolymers with excess amount of $(\text{HMe}_2\text{Si})_3\text{CLi}$. All of the obtained spectroscopic results indicate that the conversion of carbonyl groups into bis(silyl)alkene on the side chain of polymers were completely carried out. The ^1H NMR spectra of the copolymers show the complete disappearance of carbonyl proton resonance at 9.91 ppm and the concomitant appearance of Si-H protons at 3.99–4.07 ppm and –SiMe₂ protons at 0.07–0.25 ppm (Fig. 1). In addition, the FT-IR spectra of the obtained copolymers $\text{I}_{\text{Si-H}}$ and $\text{II}_{\text{Si-H}}$ do not show a sharp peak at 1696 cm^{-1} which indicates the absence of –CHO group. And also a sharp peak at 2019 cm^{-1} related to Si–H bond was observed.

3. Conclusion

A variety of non-enolizable aromatic aldehydes were converted to the corresponding 1,1-bis(silyl)-1-alkenes in one-pot procedure involving the addition of $(\text{HMe}_2\text{Si})_3\text{CLi}$ to aromatic aldehyde. It is likely that the initial step of $(\text{HMe}_2\text{Si})_3\text{CLi}$ reaction with formyl

groups proceed via nucleophilic attack at carbonyl group yielding (A) as intermediate, and then followed by an intramolecular reaction between Si–H and OLi groups of (A) resulting in ring closure and the formation of the intermediate (B) which is swiftly converted to 1,1-bis(silyl)-1-alkenes. In order to examine similar reaction on the polymer side chain, **I** and **II** random homopolymers were functionalized with formyl groups. It is found that solvent plays a crucial role in the formylation reaction. PhNO_2 appears to be a more suitable solvent than CH_2Cl_2 . Treatment of $(\text{HMe}_2\text{Si})_3\text{CLi}$ with carbonyl groups in the side chain of functionalized polymers I_{CHO} and II_{CHO} led to the preparation of new macromolecules containing Si–H groups ($\text{I}_{\text{Si-H}}$ and $\text{II}_{\text{Si-H}}$) which have potential for conversion into new materials with a variety of chemically reactive pendant groups.

4. Experimental

4.1. Solvents and reagents

The reactions involving organolithium reagents were carried out under dry argon. Solvents were dried by standard methods. Substrates for preparation of tris(dimethylsilyl)methyl lithium, viz. HSiMe_2Cl (Merck), Mg (Merck), CHBr_3 (Merck), and all benzaldehyde derivatives (Merck) and dichloromethyl ether (Cl_2CHOMe) (Merck) and tin (IV) chloride (SnCl_4) (Merck) were used as received. For the synthesis of LDA *n*-BuLi (Fluka 1.6 M) was titrated by diphenylacetic acid.

4.2. Spectra

The ^1H NMR and ^{13}C NMR were recorded with a Bruker FT-400 MHz spectrometer at room temperature and CDCl_3 as a solvent. The mass spectra were obtained with a GC-Mass Agilent, quadrupole mode 5973N instrument, operating at 70 eV. The FT-IR spectra were recorded on a Bruker-Tensor 270 spectrometer. Elemental analyses were carried out with an Elementar vario EL III instrument.

4.3. Preparation of the formylated polymers

Dissolved polymer in nitrobenzene was treated with methyl dichloromethyl ether (Cl_2CHOMe) in the presence of anhydrous tin (IV) chloride (SnCl_4) (mole ratio 1:1:2, 20–25 °C, 3 h). After hydrolysis and washing with water, 1,4-dioxane–HCl mixture, the organic layer was poured into cooled methanol to precipitate the formylated polymer.

4.4. Copolymer I_{CHO}

FT-IR (KBr, cm^{-1}), 3033 (HC=), 2840, 2731 (CHO), 1695 (CO), 1600, 1450 (Ph); ^1H NMR (400 MHz, CDCl_3 , ppm): δ 1.41–1.86 (aliphatic), 6.50–8.25 (aromatic), 9.88 (CHO).

4.5. Copolymer II_{CHO}

FT-IR (KBr, cm^{-1}), 3030 (HC=), 2844, 2732 (CHO), 1696 (CO), 1601, 1449 (Ph); ^1H NMR (400 MHz, CDCl_3 , ppm): δ 0.01–1.63 (aliphatic), 6.99–8.24 (aromatic), 9.91 (CHO).

4.6. Preparation of polymer bearing 1,1-bis(silyl)-1-alkenes

$(\text{HMe}_2\text{Si})_3\text{CLi}$ [20] (15.8 mmol) was added dropwise with stirring to solutions of copolymers I_{CHO} and II_{CHO} (15.8 mmol) in THF at room temperature. The reaction was quenched by adding a small amount of acidic methanol after 2 h and the reaction mixture

was poured into cooled acidic methanol to precipitate the polymers **I_{Si-H}** and **II_{Si-H}**.

4.7. Copolymer **I_{Si-H}**

FT-IR (KBr, cm^{-1}), 3035 (HC=), 2110 (Si-H), 1251, 895 (Si-CH₃); ¹H NMR (400 MHz, CDCl₃, ppm): δ 0.10–0.26 (dd, SiMe₂), 1.55–1.95 (aliphatic), 4.01–4.10 (Si-H), 7.05–7.30 (aromatic).

4.8. Copolymer **II_{Si-H}**

FT-IR (KBr, cm^{-1}), 3033 (HC=), 2109 (Si-H), 1250, 893 (Si-CH₃); ¹H NMR (400 MHz, CDCl₃, ppm): δ 0.07–0.25 (dd, SiMe₂), 0.500–2.27 (aliphatic), 3.99–4.07 (Si-H), 6.98–7.26 (aromatic).

4.9. General procedure for synthesis of 1,1-bis(silyl)-1-alkenes

(HMe₂Si)₃ClI (15.8 mmol) and aldehyde (15 mmol) in ether (10 ml) was refluxed for 2 h, and then poured into water and extracted into ether. The organic layer was washed with water and dried (Na₂SO₄). The solvent was evaporated to give a liquid which was separated on a preparative TLC in *n*-hexane to give 1,1-bis(silyl)-1-alkenes.

4.10. Preparation of 1,1-bis(dimethylsilyl)-2-phenylethylene

A colourless oil: *R_f* = 0.95 (*n*-hexane); yield = 74%; FT-IR (KBr, cm^{-1}), 3062 (HC=), 2114 (Si-H), 1555, 1490 (Ph) 1251, 898 (Si-CH₃); ¹H NMR (400 MHz, CDCl₃, ppm): δ 0.19 (d, 6H, ³J_{HH} = 3.82 Hz, SiMe₂), 0.31 (d, 6H, ³J_{HH} = 3.68 Hz, SiMe₂), 4.30–4.34 (m, 2H, Si-H), 7.30–7.34 (m, 5H, Ph), 7.83 (s, 1H, HC=); ¹³C NMR (100 MHz, CDCl₃, ppm): δ -4.2, -3.3 (SiMe₂), 125.3, 126.5, 127.1, 139.6, 140.0, 154.9 (Ph, C=C); *m/z* (EI): 220 (15%, [M]⁺), 205(32%, [M-Me]⁺), 161 (70%, [M-SiMe₂H]⁺), 143 (100%, [M-Ph]⁺), 59 (18%, [SiMe₂H]⁺). Anal. Calc. for C₁₂H₂₀Si₂: C, 65.4; H, 9.1. Found: C, 65.7; H, 9.3%.

4.11. Preparation of 1,1-bis(dimethylsilyl)-2-(*m*-fluorophenyl)-ethylene

A colourless oil: *R_f* = 0.78 (*n*-hexane); yield = 65%; FT-IR (KBr, cm^{-1}), 3068 (HC=), 2116 (Si-H), 1560, 1482 (Ph) 1253, 891 (Si-CH₃); ¹H NMR (400 MHz, CDCl₃, ppm): δ -0.30 (d, 6H, ³J_{HH} = 3.84 Hz, SiMe₂), -0.19 (d, 6H, ³J_{HH} = 3.68 Hz, SiMe₂), 3.78–3.83 (m, 2H, Si-H), 6.48–6.60 and 6.79–6.84 (m, 4H, Ph), 7.30 (s, 1H, HC=); ¹³C NMR (100 MHz, CDCl₃, ppm): δ -4.0, -3.4 (SiMe₂), 113.3, 113.9, 122.9, 142.1, 128.3, 153.3, 160.2, 162.7 (Ph, C=C); *m/z* (EI): 238 (15%, [M]⁺), 223 (32%, [M-Me]⁺), 219 (10%, [M-F]⁺), 179 (85%, [M-SiMe₂H]⁺), 163 (100%, [M-F-SiMe₂H]⁺), 154 (35%, [M-C₆H₄F]⁺), 59 (20%, [SiMe₂H]⁺). Anal. Calc. for C₁₂H₁₉Si₂F: C, 60.5; H, 8.0. Found: C, 60.7; H, 8.2%.

4.12. Preparation of 1,1-bis(dimethylsilyl)-2-(*m*-chlorophenyl)-ethylene

A colourless oil: *R_f* = 0.85 (*n*-hexane); yield = 68%; FT-IR (KBr, cm^{-1}), 3063 (HC=), 2115 (Si-H), 1559, 1470 (Ph) 1255, 895 (Si-CH₃); ¹H NMR (400 MHz, CDCl₃, ppm): δ 0.16 (d, 6H, ³J_{HH} = 3.86 Hz, SiMe₂), 0.27 (d, 6H, ³J_{HH} = 3.68 Hz, SiMe₂), 4.24–4.29 (m, 2H, Si-H), 7.14–7.27 (m, 4H, Ph), 7.70 (s, 1H, HC=); ¹³C NMR (100 MHz, CDCl₃): δ -4.0, -3.4 (SiMe₂), 125.2, 126.5, 127.2, 128.0, 132.8, 141.5, 142.4, 153.1 (Ph, C=C); *m/z* (EI): 256 (3%, [M+2]⁺), 254 (9%, [M]⁺), 239 (57%, [M-Me]⁺), 219 (10%, [M-Cl]⁺), 195 (85%, [M-SiMe₂H]⁺), 143 (100%, [M-Cl-SiMe₂H]⁺), 59 (20%, [SiMe₂H]⁺). Anal. Calc. for C₁₂H₁₉Si₂Cl: C, 56.7; H, 7.5. Found: C, 56.5; H, 7.3%.

4.13. Preparation of 1,1-bis(dimethylsilyl)-2-(*p*-chlorophenyl)ethylene

A colourless oil: *R_f* = 0.85 (*n*-hexane); yield = 60%; FT-IR (KBr, cm^{-1}), 3060 (HC=), 2114 (Si-H), 1555, 1468 (Ph) 1250, 892 (Si-CH₃); ¹H NMR (400 MHz, CDCl₃, ppm): δ 0.16 (d, 6H, ³J_{HH} = 3.78 Hz, SiMe₂), 0.27 (d, 6H, ³J_{HH} = 3.38 Hz, SiMe₂), 4.20–4.29 (m, 2H, Si-H), 7.20–7.23 (d, ³J_{HH} = 8.59 Hz, 2H, Ph), 7.27–7.29 (d, ³J_{HH} = 8.34 Hz, 2H, Ph), 7.70 (s, 1H, HC=); ¹³C NMR (100 MHz, CDCl₃, ppm): δ -4.0, -3.4 (SiMe₂), 126.4, 127.0, 127.6, 128.5, 142.9, 153.4 (Ph, C=C); *m/z* (EI): 256 (6%, [M+2]⁺), 254 (18%, [M]⁺), 239 (45%, [M-Me]⁺), 219 (14%, [M-Cl]⁺), 195 (100%, [M-SiMe₂H]⁺), 143 (59%, [M-Cl-SiMe₂H]⁺), 59 (36%, [SiMe₂H]⁺). Anal. Calc. for C₁₂H₁₉Si₂Cl: C, 56.7; H, 7.5. Found: C, 56.4; H, 7.1%.

4.14. Preparation of 1,1-bis(dimethylsilyl)-2-(2,6-dichlorophenyl)-ethylene

A colourless oil: *R_f* = 0.78 (*n*-hexane); yield = 56%; FT-IR (KBr, cm^{-1}), 3056 (HC=), 2119 (Si-H), 1562, 1427 (Ph) 1251, 889 (Si-CH₃); ¹H NMR (400 MHz, CDCl₃, ppm): δ 0.06 (d, 6H, ³J_{HH} = 3.84 Hz, SiMe₂), 0.34 (d, 6H, ³J_{HH} = 3.69 Hz, SiMe₂), 3.89–3.92 (m, 1H, Si-H), 4.33–4.36 (m, 1H, Si-H), 7.14–7.18 (t, 1H, ³J_{HH} = 8.01 Hz, Ph), 7.31–7.33 (d, 2H, ³J_{HH} = 8.01 Hz, Ph), 7.39 (s, 1H, HC=); ¹³C NMR (100 MHz, CDCl₃, ppm): δ -4.5, -4.5 (SiMe₂), 126.5, 127.4, 127.6, 137.6, 145.4, 147.6 (Ph, C=C); *m/z* (EI): 293 (1% [M+4]⁺), 291 (6%, [M+2]⁺), 289 (9%, [M]⁺), 274 (14%, [M-Me]⁺), 142 (100%, [M-Ph-2Cl]⁺), 59 (36%, [SiMe₂H]⁺). Anal. Calc. for C₁₂H₁₈Si₂Cl₂: C, 49.8; H, 6.2. Found: C, 50.1; H, 6.5%.

4.15. Preparation of 1,1-bis(dimethylsilyl)-2-(*o*-boromophenyl)-ethylene

A colourless oil: *R_f* = 0.80 (*n*-hexane); yield = 54%; FT-IR (KBr, cm^{-1}), 3033 (HC=), 2118 (Si-H), 1590, 1489 (Ph) 1255, 895 (Si-CH₃); ¹H NMR (400 MHz, CDCl₃, ppm): δ -0.37 (d, 6H, ³J_{HH} = 3.84 Hz, SiMe₂), -0.12 (d, 6H, ³J_{HH} = 3.72 Hz, SiMe₂), 3.69–3.73 (m, 1H, Si-H), 3.87–3.90 (m, 1H, Si-H), 6.67–7.10 (m, 4H, Ph), 7.26 (s, 1H, HC=); ¹³C NMR (100 MHz, CDCl₃, ppm): δ -4.3, -4.1 (SiMe₂), 121.8, 125.6, 127.9, 128.9, 131.1, 140.1, 141.7, 154.0 (Ph, C=C); *m/z* (EI): 301 (5%, [M+2]⁺), 299 (5%, [M]⁺), 284 (7%, [M-Me]⁺), 219 (30%, [M-Br]⁺), 143 (100%, [M-C₆H₄Br]⁺), 59 (20%, [SiMe₂H]⁺). Anal. Calc. for C₁₂H₁₉Si₂Br: C, 48.2; H, 6.3. Found: C, 48.5; H, 6.4%.

4.16. Preparation of 1,1-bis(dimethylsilyl)-2-(*p*-boromophenyl)-ethylene

A colourless oil: *R_f* = 0.80 (*n*-hexane); yield = 52%; FT-IR (KBr, cm^{-1}), 3030 (HC=), 2116 (Si-H), 1590, 1489 (Ph) 1255, 895 (Si-CH₃); ¹H NMR (400 MHz, CDCl₃, ppm): δ -0.26 (d, 6H, ³J_{HH} = 3.84 Hz, SiMe₂), -0.15 (d, 6H, ³J_{HH} = 3.68 Hz, SiMe₂), 3.84–3.87 (m, 2H, Si-H), 6.72 (d, ³J_{HH} = 8.41 Hz, 2H, Ph), 7.02 (d, ³J_{HH} = 8.41 Hz, 2H, Ph), 7.26 (s, 1H, HC=); ¹³C NMR (100 MHz, CDCl₃, ppm): δ -4.0, -3.4 (SiMe₂), 120.6, 128.8, 129.9, 138.5, 141.5, 153.4 (Ph, C=C); *m/z* (EI): 301 (7%, [M+2]⁺), 299 (7%, [M]⁺), 284 (35%, [M-Me]⁺), 219 (25%, [M-Br]⁺), 143 (100%, [M-C₆H₄Br]⁺), 59 (30%, [SiMe₂H]⁺). Anal. Calc. for C₁₂H₁₉Si₂Br C, 48.2; H, 6.3. Found: C, 47.9; H, 6.1%.

References

- [1] P. Pawluc, G. Hreczycho, B. Marciniak, J. Org. Chem. 71 (2006) 8676.
- [2] G. Hreczycho, P. Pawluc, B. Marciniak, Synthesis 8 (2006) 1370.
- [3] D.M. Hodgson, P.J. Comina, M.G.B. Drew, J. Chem. Soc., Perkin Trans. 1 (1997) 2279.
- [4] G.A. Molander, J.A.C. Romero, C.P. Corrette, J. Organomet. Chem. 647 (2002) 225.

- [5] J. Konodo, A. Inoue, H. Shinokubo, K. Oshima, *Tetrahedron Lett.* 43 (2002) 2399.
- [6] I. Marek, *Chem. Rev.* 100 (2000) 2887.
- [7] H. Ohmiya, H. Yorimitsu, K. Oshima, *Angew. Chem., Int. Ed.* 44 (2005) 3488.
- [8] K.D. Safa, S. Paymard Samani, S. Tofangdarzadeh, A. Hassanpour, *J. Organomet. Chem.* 693 (2008) 2004.
- [9] K.D. Safa, M.H. Nasirtabrizi, *Eur. Polym. J.* 41 (2005) 2310.
- [10] K.D. Safa, M. Babazadeh, H. Namazi, M. Mahkam, M.G. Asadi, *Eur. Polym. J.* 40 (2004) 459.
- [11] K.D. Safa, M. Babazadeh, *e-Polymers* 16 (2004).
- [12] K.D. Safa, M. Babazadeh, *Eur. Polym. J.* 40 (2004) 1659.
- [13] A. Kowalewaska, W.A. Stanczyk, S. Boileau, L. Lestel, J.D. Smith, *Polymer* 40 (1999) 813.
- [14] D.J. Peterson, *J. Org. Chem.* 33 (1968) 780.
- [15] M.L. Kwan, M.A. Battiste, *Tetrahedron Lett.* 43 (2002) 8765.
- [16] K. Itami, T. Nokami, J. Yoshida, *Org. Lett.* 2 (2000) 1299.
- [17] I. Fleming, C.D. Floyd, *J. Chem. Soc., Perkin Trans. 1* (1997) 969.
- [18] K.D. Safa, M. Shahrivar, Sh. Tofangdarzadeh, A. Hassanpour, *Tetrahedron* 63 (2007) 3189.
- [19] K.D. Safa, Sh. Tofangdarzadeh, H. Heydari Ayenadeh, *Heteroatom Chem.* 19 (2008) 365.
- [20] J. Eric, F. Hawrelak, T. Ladipo, *Organometallics* 18 (1999) 1804.
- [21] J. Kahovec, *Polym. Bull.* 4 (1981) 731.