Highly Stereoselective Synthesis of Arylene-Silylene-Vinylene Polymers

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Dedicated to Professor Julian Chojnowski on the occasion of his 70th birthday in recognition of his significant contribution to organosilicon polymer chemistry.

Abstract: Stereoregular *trans*-arylene-silylene-vinylene polymers of $M_w = 13100-34800$ and PDI = 1.6–2.9 of the general formulas $CH_2{=}CH-[-SiMe_2C_6H_4\text{-}SiMe_2CH{=}CH-]-$(**16**, **17**, **18**) and $CH_2{=}CH-[-(R)CH{=}CHC_6H_4CH{=}CH-]-$(where $R = -Me_2Si\text{-}p\text{-}C_6H_4\text{-}SiMe_2-$, $-Me_2Si\text{-}m\text{-}C_6H_4SiMe_2-$ and $-Me_2SiC_6H_4\text{-}C_6H_4SiMe_2-$) (**19**, **20**, **21**) have been effectively synthesized *via* silylative coupling (SC) homopolycondensation of bis(vinyldimethylsilyl)arenes (**10**, **12**, **14**) and cross-polycondensation of 4-(vinyldimethylsilyl)styrene (**11**) as well as cross-copolycondensation of bis(vinyldimethylsilyl)arenes (**10**, **12** and **14**) with 1,4-divinylbenzene (**9**) catalyzed by $[RuH(Cl)(CO)(PCy_3)_2]$ (**7**). Such highly stereoregular products cannot be synthesized *via* ADMET polycondensation or ring opening metathesis ROM or polyaddition of hydridosilanes to acetylenes.

Keywords: arylene-silylene-vinylene polymers; homogeneous catalysis; polycondensation; ruthenium; silylative coupling

Introduction

Polymers with silylene-bridged π-conjugated systems have recently received a lot of attention because of their potential usefulness in opto-electronic functional materials.[1–3] In particular arylene-silylene-vinylene polymers have been reported to show interesting photophysical properties.[4] The introduction of silicon atoms into π-conjugated systems seems to raise the LUMO of the π-conjugated systems, and improves their solubility and processibility due to increased flexibility. Moreover, the presence of Si-atoms reduces the barrier injection and transportation processes, in comparison with those of other polymers containing saturated spacer groups.[5]

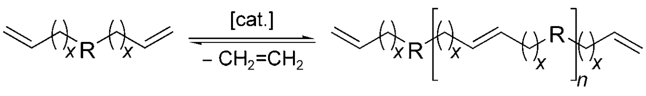
Polymers containing phenylene-silylene-vinylene units are usually synthesized by Pt- and Rh-catalyzed hydrosilylation,[6] but the polymer-chain structures were present as a mixture of *gem*-, *cis*-1,2- and *trans*-1,2-isomeric fragments.

One of the ways of the synthesis of unsaturated silicon oligomers and polymers is acyclic diene metathesis (ADMET) polymerization of silicon-containing dienes such as dialkenylenes and siloxanes (with the exception of divinyl derivatives), occurring smoothly in the presence of highly active metallacarbenes (M = W, Mo, Ru) (for recent reviews, see[7,8]). These unsaturated homopolymers, which include carbosilane and carbosiloxane units, can be synthesized using this methodology[9] (Scheme 1).

As opposed to the aforesaid monomers, the vinyl derivatives of silicon compounds are completely inert to productive homometathesis due to steric and electronic effects of the silyl group stimulating non-productive cleavage of metalla-cyclobutane intermediate containing two silyl groups attached to adjacent carbon atoms.[10]

However, in the presence of ruthenium complexes which contain or generate [Ru–H] and [Ru–Si] bonds, such compounds as divinylsilanes,[11,12] divinyldisiloxanes,[11,12] divinyldisilazane[13] and bis(vinylsilyl)alkanes[14] undergo a silylative coupling (SC) polycondensation to linear products according to Scheme 2 (for a recent review, see[8]).

Furthermore, we have also reported preliminary results for the synthesis of homopolymers containing phe-



where: $R = -SiMe_2-$; $-Me_2Si\text{-}O\text{-}SiMe_2-$; $x > 0$.

Scheme 1.

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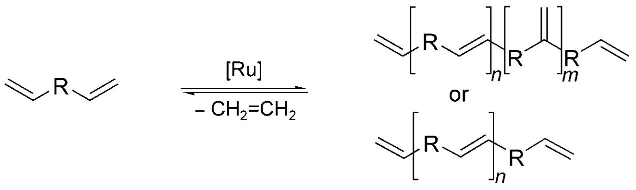


where: R = -SiMe$_2$-; -SiPh$_2$-; -Me$_2$Si-O-SiMe$_2$-; -OEt$_2$Si-O-SiOEt$_2$-;
-Me$_2$Si-NH-SiMe$_2$-; -SiMe$_2$-(CH$_2$)$_n$-SiMe$_2$-;

Scheme 2.

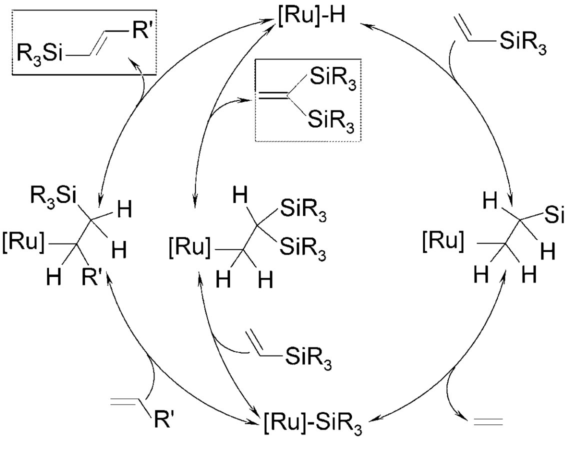
nylene-silylene-vinylene and copolymers consisting of phenylene-silylene-vinylene-phenylene-vinylene fragments with well-defined structures[17] which are of growing interest due to their efficient photo- and electroluminescence properties.[4,16]

Under suitable conditions, the mechanism of silylative coupling reaction of monovinylsilanes is well-established (for reviews, see[7,8,15] and involves a cleavage of the carbon-silicon (=C–Si) bond of the vinylsilane and the carbon-hydrogen (=C–H) bond of the olefin (e.g., styrene) or a second vinylsilane molecule (in the silylative *homo*-coupling) as shown in Scheme 3, for the stereoselective synthesis of *trans*-product.

The aim of this work was to apply silylative coupling (SC) polycondensation as a new synthetic route to prepare regio- and stereoselectively *trans*-polymeric materials, poly(arylene-silylene-vinylene)s.

Results and Discussion

Although different ruthenium complexes have been used for the silylative coupling reaction of various olefins, their reactivity and selectivity have not been directly compared, since the reactions have been performed under different conditions (temperature, ratio of substrates, substituted at silicon, etc.).



where: R = alkyl, aryl, alkoxyl, siloxyl; R' = Ph or SiR'$_3$

Scheme 3. Mechanism of silylative coupling reaction of vinylsilanes catalyzed by ruthenium complexes.

For the synthesis of homopolymers having the arylene-silylene-vinylene unit we have made several catalytic tests of the following model reaction – the silylative *homo*-coupling process of vinylphenyldimethylsilane (whose structure is similar to the fragments of chains of the desired polymers) catalyzed by five- and six-coordinated ruthenium catalysts, according to the Scheme 4.

Many ruthenium complexes have been tested in the silylative-coupling reaction. The basic assumption of the synthetic procedure requires the absence of *gem*-product. The results are presented in Table 1, along with those reported earlier on silylative coupling occurring in the presence of different catalysts and under different conditions.

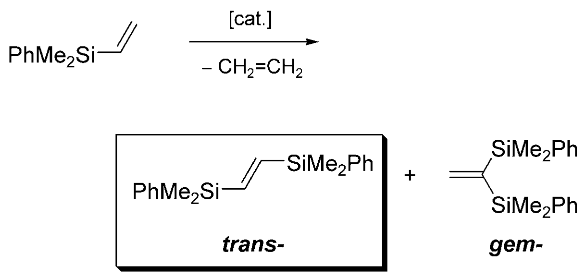
The catalysis of the initial hexacovalent ruthenium complexes (**2**, **3**, **4**, **5** and **8**) was less effective than in the presence of pentacoordinated (**6** and **7**) species, i.e., coordinatively unsaturated. Obviously, the catalytic activities of complexes **6** and **7** are very similar but when the silyl-ruthenium complex (**6**) is used a significant amount of *gem*-product was also observed.

In this case, we selected more active catalysts from this group – dimeric ruthenium (**1**) and two ruthenium phosphine complexes (**6**, **7**) – and used them in preliminary catalytic tests in order to choose the best conditions for selective synthesis of a well-defined *trans*-polymer. The results are presented in Table 2.

While the catalyst **6** gave a mixture of *trans*-1,2-isomeric fragments and 1,1-isomeric fragments the catalysts **1** and **7** gave only *trans*-isomeric derivatives. Therefore, we used the [RuH(Cl)(CO)(PCy$_3$)$_2$] complex **7** as a catalyst for a long-time reaction occurring according to Scheme 5, to obtain polymers with rather high average molecular weight and low polydispersity index.

The structures of the obtained polymers were characterized and determined by ^{1}H, ^{13}C and ^{29}Si NMR as well as IR and Raman spectroscopy. The absence of fragments with a quaternary carbon atom was also revealed by DEPT spectroscopic analysis. The ^{13}C NMR and DEPT spectra are shown in Figs. 1 and 2, respectively.

Similarly, in order to synthesize a homopolymer consisting of arylene-silylene-vinylene-phenylene-vinylene



Scheme 4. Model reaction of silylative coupling of vinylphenyldimethylsilane.

Table 1. Effect of catalyst on the conversion of vinylphenyldimethylsilane and chemo-selectivity process.

Catalyst		Conversion of $VinSiMe_2Ph$ [%][a]	Yield of products[b] [%]	
			[*trans*-] : [*gem*-]	
$\{[Ru(\mu\text{-}Cl)_2(CO)_3]\}_2$	**(1)**	53	512	2
$[RuH(Cl)(CO)(PPh_3)_3]$	**(2)**	74	72	2
$[RuH(Cl)(CO)_2(PPh_3)_2]$	**(3)**	36	36	–
$[RuH(OAc)(CO)(PPh_3)_2]$	**(4)**	16	16	–
$[RuH(OAc)(PPh_3)_3]$	**(5)**	11	10	1
$[Ru(SiMe_3)(Cl)(CO)(PPh_3)_2]$	**(6)**	85	78	7
$[RuH(Cl)(CO)(PCy_3)_2]$	**(7)**	85	85	–
$[RuH(OAc)(CO)(PCy_3)_2]$	**(8)**	13	13	–

[a] Conversion calculated from GC.

[b] Calculated from GC and identified by use GC-MS and NMR methods.

– Not observed.

Reaction conditions: [VinSi]:[Ru] = 100:1, in toluene (1 M), under Ar, 18 h, 110 °C.

Table 2. Catalytic tests for polycondensation of 1,4-bis(vinyldimethylsilyl)benzene (**10**).

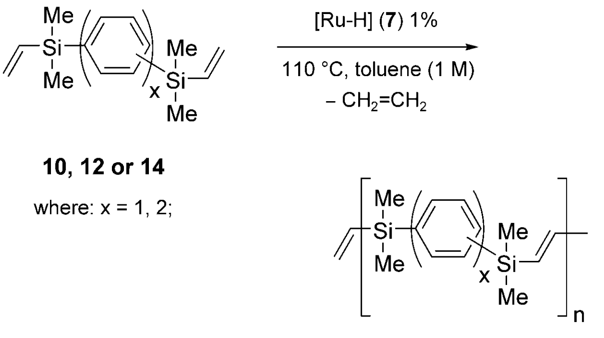
Catalyst	Conversion of monomer [%][a]	Ratio of products [%][b]			Selectivity [%][c]	
		Dimer	Trimer	Oligomers	[1,2-]/[1,1-]	
1	86	23	22	55	>99	0
6	92	17	21	62	75	25
7	97	12	16	72	>99	0

[a] Conversion calculated from GC.

[b] Identified by use GC-MS and GPC.

[c] Calculated from ^1H NMR.

Reaction conditions: [monomer]:[cat.] = 100:1, in toluene (1 M), 24 h, 110 °C, under Ar.



Scheme 5. General scheme of silylative coupling (SC) polycondensation of bis(vinyldimethylsilyl)arenes (**10, 12, 14**) in the presence of complex **7**.

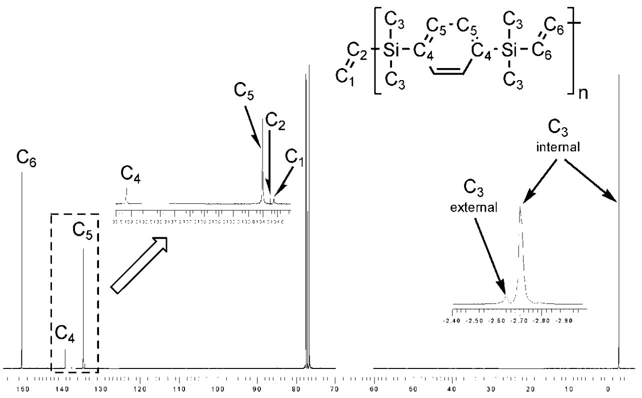


Figure 1. ^{13}C NMR spectrum of homopolymer **16** in $CDCl_3$.

units, various ruthenium complexes have been tested for the silylative *cross*-coupling reaction. The catalytic screenings have been carried out in the model catalytic process of vinyldimethylphenylsilane with styrene.[20]

The regio- and stereoregular *trans*-homopolymer **15** was effectively prepared by polycondensation of **11** (monomer which consists of two functional groups: vinylsilyl and styryl) using the very effective and active ruthenium complex **7** as a catalyst, see Scheme 6.

The structure of its main chain was a result of a 'head-to-tail' polycondensation reaction. The next issue of our interest was the synthesis of unsaturated organosilicon copolymers. Like in the case of establishing the reaction conditions for the synthesis of homopolymers, we car-

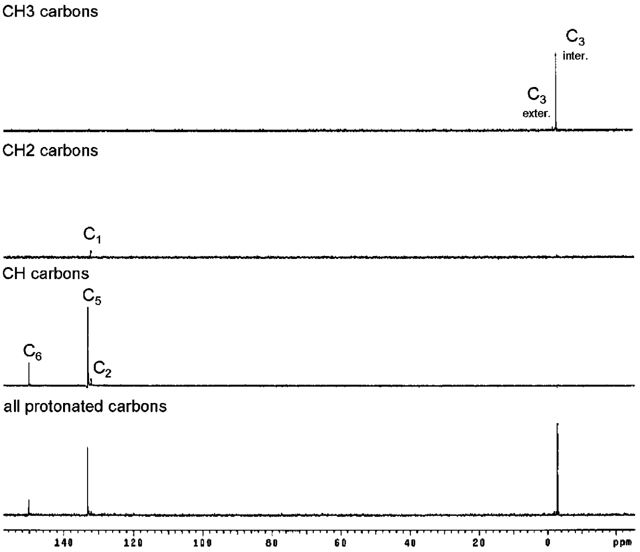
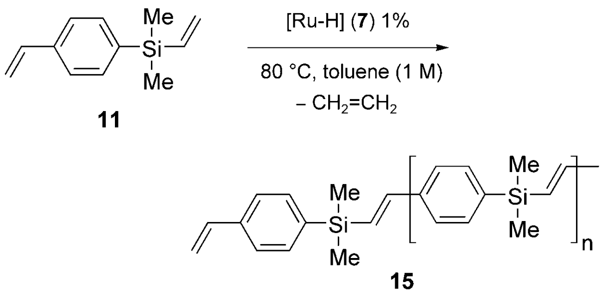


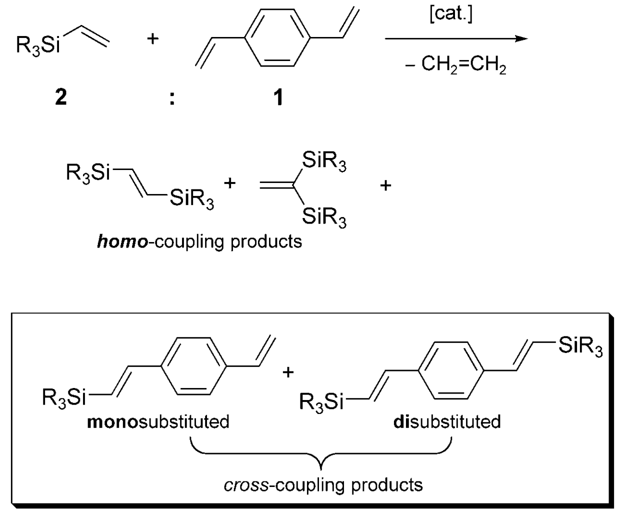
Figure 2. DEPT spectrum of homopolymer **16**.



Scheme 6. Scheme of silylative *cross*-coupling (SC) polycondensation of 4-(vinyldimethylsilyl)styrene (**11**) in the presence of catalyst **7**.

ried out preliminary catalytic tests using chosen ruthenium complexes, according to the Scheme 7:

The results are presented in Table 3. It has been found that only one catalyst, complex **7**, is the best for the preparation of well-defined copolymers.



Scheme 7. Model reaction of silylative *cross*-coupling of vinylsilanes with 1,4-divinylbenzene (**9**).

Complex **7** catalyzes chemoselectively this coupling reaction to obtain exclusively *trans*-stereoproducts. Thus, copolymers **19**, **20**, and **21** were synthesized by copolycondensation *via* silylative-*cross*-coupling reaction of bis(vinyldimethylsilyl)arene derivative monomers (**10**, **12** and **14**) with DVB (**9**) under the conditions presented in Scheme 8.

In the above reaction conditions we have never observed uncontrolled radical polymerization of 1,4-divinylbenzene.

The chemical structures of the products were verified by methods described in the experimental section. The analytical data allowed us to propose linear and *trans*-(stereo)regular structures of the polymeric materials obtained with perfect consecutive arylene-silylene-vinylene or arylene-silylene-vinylene-phenylene-vinylene linkages. The results of spectroscopic analyses of all products obtained in the presence of this catalyst excluded the occurrence of quaternary carbons $[(-\mathrm{SiMe_2})_2C{=}\mathrm{CH_2})]$ in the polymer's main chains. Ex-

Table 3. Effect of catalyst on the conversion of DVB (**9**), vinylsilanes and chemoselectivity of the process.

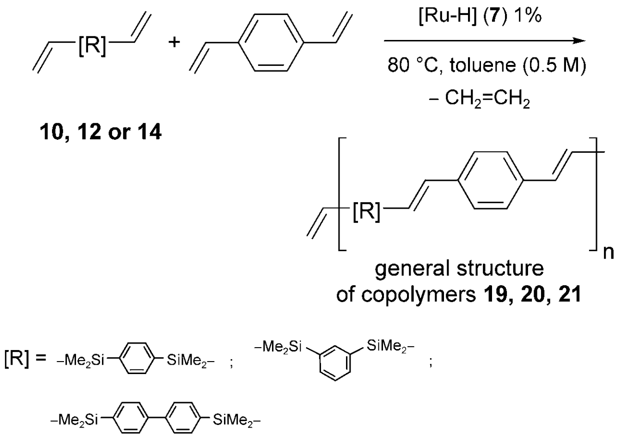
Vinylsilane	Catalyst	Conversion of DVB [%][a]	Conversion of VinSi [%][a]	Yield of products [%][b]		
				homo-	mono-	di-
$\mathrm{VinSiMe_2Ph}$	**2**	84	71	4	34	50
	6	92	69	8	54	38
	7	97	91	–	12	85
$\mathrm{VinSiMe_2C_{12}H_9}$	**2**	80	66	2	33	47
	6	86	68	5	46	40
	7	95	88	–	14	81

[a] Conversion calculated from GC.

[b] Calculated from GC and identified by use GCMS and NMR methods.

– Not observed.

Reaction conditions: [VinSi]:[DVB]:[Ru] = 200:100:1, in toluene (0.5 M), under Ar, 18 h, 80 °C.



Scheme 8. General scheme of silylative *cross*-coupling (SC) copolycondensation of bis(vinyldimethylsilyl)arenes (**10**, **12**, **14**) with 1,4-divinylbenzene (**9**) in the presence of catalyst **7**.

amples of proton spectra of homopolymer **16** and copolymer **21**, which prove the purity of the structures of the final products (Fig. 3 and Fig. 4) are shown below.

For all homopolymers **16**, **17** and **18** we have identified single signals (adequately: 6.82, 6.84 and 6.88 ppm) corresponding with *homo*-coupling fragments (–SiC*H*=C*H*Si–).

However, for copolymers **19**, **20** and **21**, the ^{1}H NMR spectra showed us two characteristic, double signals (–Si–CH=C*H*–C< and –Si–C*H*=CH–C>) with coupling constant $J_{H,H}$ from 19.0 Hz to 19.2 Hz, typical for the *trans* isomer only.

The yields and molecular weights of the final products are listed in Table 4. The yields (after isolation) of polymers are between 78 and 92%.

The molecular weights of **15**, **16** and **19** are higher than those of the previously reported polymers[17] (characterizing similar structures). The typical GPC traces of exemplary products **15**, **19**, **20**, **21** are presented in Figure 5.

The calculated polydispersity (PDI) of the polymers was in the range between 1.6 and 2.9 (see Table 4).

The thermal stability of the polymers was ascertained on the basis of thermogravimetric analysis (TGA), see Table 4. As follows from the TGA thermal analysis profiles (Fig. 6), the polymers started to lose weight near 100 °C for **17**, 198 °C for **16** and very similarly for **18**, 115 °C for **19**, 240 °C for **20** and 265 °C for **15** and **21**, and the maximum decomposition rate was between 414 °C and 599 °C in the TGA experiment (Figure 6). The final residue yields were in the range 53–77% at 900 °C.

Although the overall trends are very similar, early-stage decomposition profiles differ, depending on the arene structure: that with biphenylene fragment **21** is more stable than those with phenylene units. The T_{d10} (temperature showing 10% weight loss) can be conveniently employed to quantify the difference (Figure 6). The results are summarized in Table 4. The parameter Td_{10} revealed the difference of about 27 °C between the two types of polymers. This indicated that polymer **15** is more stable than copolymers **19** and **12**, but similar to copolymer **21**. The photophysical properties of these polymeric materials have been understudied.

Conclusion

The first stereoregular *trans*-arylene-silylene-vinylene polymers (M_w = 13100–34800 and PDI = 1.6–2.9) can be effectively synthesized *via* silylative coupling (SC) catalyzed by [RuH(Cl)(CO)(PCy$_3$)$_2$] (**7**):

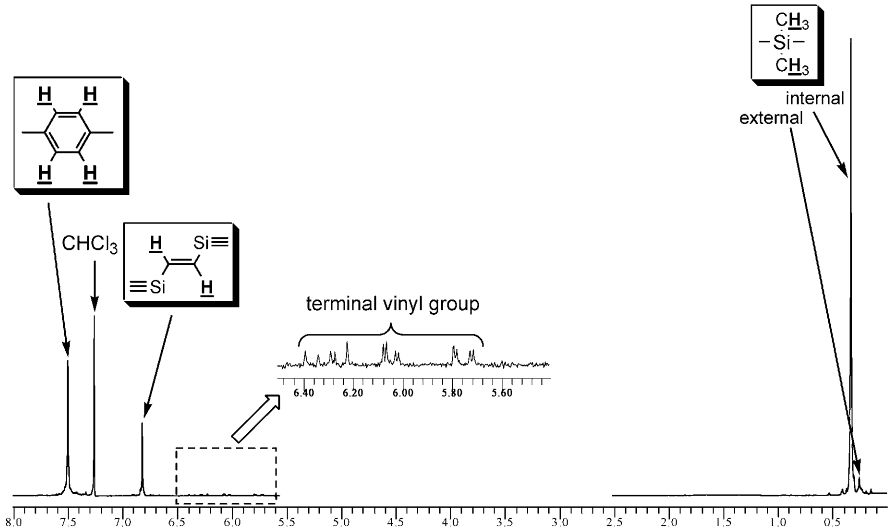


Figure 3. ^{1}H NMR spectrum of homopolymer **16** in CDCl$_3$.

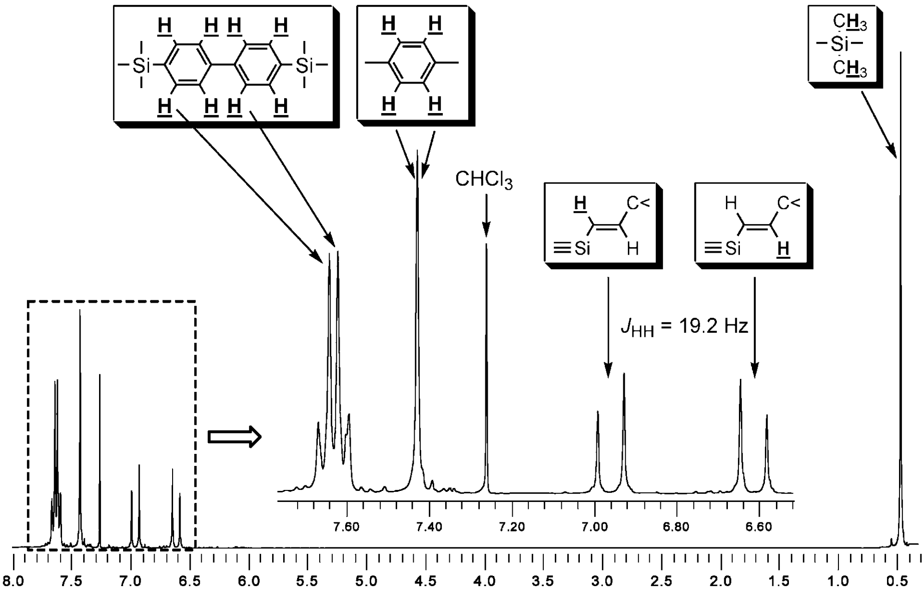


Figure 4. ^1H NMR spectrum of copolymer **21** in $CDCl_3$.

Table 4. The results of silylative coupling polycondensation reaction and thermal properties of silicon-containing arylene-silylene-vinylene polymers.

Polymer	Yield [%][a]	$M_w \times 10^4$ [b]	M_w/M_n [b]	n[c]	T_{d10} [°C][d]	Wt loss [%][e]
15	88	1.84	2.1	55	491	53
16	89	1.63	1.6	47	447	53
17	85	1.64	1.7	44	433	77
18	92	3.48	2.5	47	486	57
19	89	1.76	2.0	28	464	61
20	78	1.31	2.2	18	473	55
21	94	2.46	2.9	21	478	62

[a] Yield after isolation.
[b] M_w and PDI were determined by GPC using polystyrene standards.
[c] Calculated from GPC and compared ^1H NMR.
[d] Temperature of 10% weight loss.
[e] Weight loss in the range 25–900 °C under N_2.

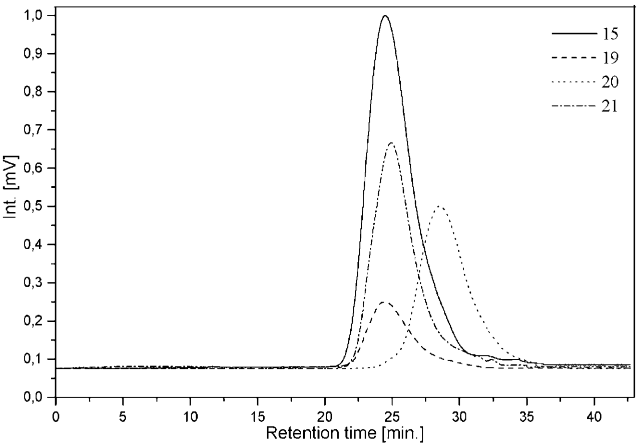


Figure 5. GPC chromatograms of polymers **15**, **19**, **20**, **21** in THF.

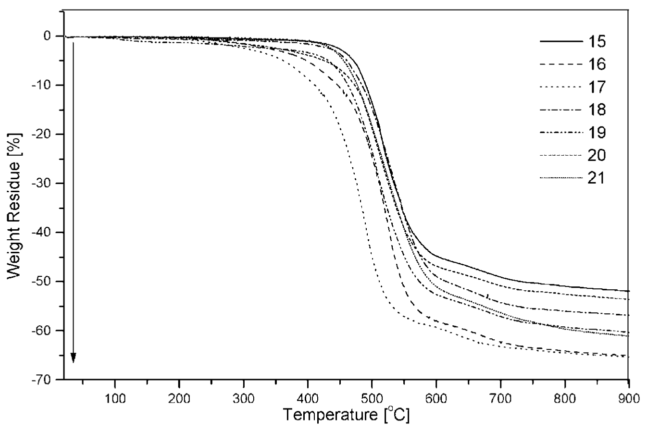


Figure 6. TGA thermal analysis profiles for homopolymers and copolymers.

- homopolycondensation of bis(vinyldimethylsilyl)arenes (**10, 12** and **14**),
- cross-polycondensation of 4-(vinyldimethylsilyl)styrene (**11**),
- cross-copolycondensation of bis(vinyldimethylsilyl)-arenes (**10, 12** and **14**) with 1,4-divinylbenzene (**9**).

The structures of the polymers were characterized and determined by ^{1}H, ^{13}C and ^{29}Si NMR as well as FTIR spectroscopy. The absence of fragments with quaternary carbon atoms [$(-SiMe_2)_2C=CH_2)$] in the chains of each polymer was also confirmed by DEPT spectroscopic analysis.

The polymeric products cannot be synthesized *via* ADMET polymerization process due to the stereoelectronic effect of silyl groups in vinyl-silicon compounds, therefore SC polycondensation opens a new synthetic route to regio- and stereoregular arylene-silylene-vinylene type polymers.

Experimental Section

General Remarks

All syntheses of monomers, polymers and catalytic tests were carried out under an inert argon atmosphere. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), ^{29}Si NMR (60 MHz) and DEPT spectra were recorded on Varian XL 300 MHz spectrometer in $CDCl_3$. Mass spectra of the monomers were obtained by GC-MS analysis (Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and an ion trap detector. High-resolution mass spectroscopic (HR-MS) analyses were performed on an AMD-402 instrument. GC analyses were performed on a Varian 3400 with a Megabore column (30 m) and TCD. Infrared spectra (film) were recorded on an FT-IR Bruker JFS-113v. Gel permeation chromatography (GPC) analysis was carried out using a Gilson HPLC system equipped with UV absorbance detector and RI detector. The GPC was equipped with a phenogel column 300 × 7.80 mm, 50, 500, 10^4 Å (analysis condition: mobile phase: THF; flow rate: 0.7 mL/min; temperature: ambient; injection volume: 20 μL). Molecular weight and dispersity indices were determined by polystyrene standard calibration. TGA analysis was carried out under nitrogen flow at heating rate of 10 °C min^{-1} on a Setaram Setsys 12 instrument with a model Setsoft version 154D data analysis software program (the temperature range of analysis was 25–1100 °C). The chemicals were obtained from the following sources: THF, toluene, methanol, methylene chloride, 1,2-dibromoethane, 4-methoxyphenol were purchased from Fluka, $CDCl_3$ from Dr Glaser A. G. Basel, chlorodimethylvinylsilane and vinylphenyldimethylsilane from Gelest. All the halogenated aryl derivatives and vinyl bromide were bought from Aldrich. The dimeric complex $\{[Ru(\mu-Cl)_2(CO)_3]\}_2$ (**1**) was purchased from Stream. CH_2Cl_2 was additionally passed through a column with aluminium oxide. The ruthenium complexes: $[RuH(Cl)(CO)(PPh_3)_3]$[18b] (**2**), $[RuH(Cl)(CO)_2(PPh_3)_2]$[18c] (**3**), $[RuH(OAc)(CO)(PPh_3)_2]$[18d] (**4**), $[RuH(OAc)(PPh_3)_3]$[18e] (**5**), $[Ru(SiMe_3)(Cl)(CO)(PPh_3)_2]$[18f] (**6**), $[RuH(Cl)(CO)(PCy_3)_2]$[18a] (**7**), $[RuH(OAc)(CO)(PCy_3)_2]$[18c] (**8**) were prepared on the basis of the procedure described in the above-cited literature. Pure 1,4-divinylbenzene, DVB (**9**) was synthesized by the Ni-catalyzed coupling reaction[19] between vinyl bromide and 1,4-bis(bromomagnesium)benzene. Monomeric 1,4-bis(vinyldimethylsilyl)benzene **(10)** was prepared according to a literature procedure.[17a]

Syntheses of Organosilicon Monomers

4-(Vinyldimethylsilyl)styrene **(11):** A solution of 4-bromostyrene (6.1 g, 33.3 mmol) in 50 mL of THF was added slowly dropwise to a suspension of Mg (1.05 g, 43.2 mmol, whose surface was activated by use of 1,2-dibromomethane, 50 μL) and vinyldimethylchlorosilane (4.41 g, 36.6 mmol) in 20 mL of THF (the mixture was lightly warmed, 20–30 °C). After the addition was completed, the reaction mixture was heated at 40 °C for 1 hour and then it was cooled at room temperature, 1 mL of water was added and the reaction mixture was filtered off. The organic solvent was removed, and the residue was distilled under reduced pressure (in the presence of 4-methoxyphenol) to afford **11** as a colourless liquid; yield: 5.33 g (85%); bp 66–67 °C/5 mmHg. ^{1}H NMR ($CDCl_3$): $\delta = 0.34$ (s, 6H, CH_3), 5.23 (d, 1H, $J = 10.8$ Hz, $>C-CH=CH_2$), 5.75 (dd, 1H, $J = 3.9$, 19.6 Hz, $SiCH=CH_2$), 5.76 (d, 1H, $J = 16.9$ Hz, $>C-CH=CH_2$), 6.05 (dd, 1H, $J = 3.8$, 14.9 Hz, $SiCH=CH_2$), 6.28 (dd, 1H, $J = 15$, 19.5 Hz, $SiCH=CH_2$), 6.71 (dd, 1H, $J = 10.8$, 17.1 Hz, $>C-CH=CH_2$), 7.4 [d, 1H, $J = 3$ Hz, $H_2C=CH-(m-C_6H_4)$], 7.5 [d, 1H, $J = 3$ Hz, $H_2C=CHSi-(o-C_6H_4)$]; ^{13}C NMR ($CDCl_3$): $\delta = -2.50$ (CH_3), 114.70 ($H_2C=CH-C_6H_4-$), 126.08 ($H_2C=CH-C_6H_4$), 133.38 ($SiCH=CH_2$), 134.59 ($-C_6H_4-SiCH=CH_2$), 137.36 ($H_2C=CH-C_6H_4-$), 138.41 ($SiCH=CH_2$), 138.54 ($H_2C=C-C<$), 138.69 ($>C-SiCH=CH_2$); ^{29}Si NMR ($CDCl_3$): $\delta = -10.22$; HR-MS: $m/z = 188.10223$; calcd. for $C_{12}H_{16}Si$: 188.10213.

1,3-Bis(vinyldimethylsilyl)benzene **(12):** A solution of 1,3-dibromobenzene (5 g, 21.2 mmol) in 45 mL of THF was added slowly dropwise to a suspension of Mg (1.29 g, 53.0 mmol, whose surface was activated by use of 1,2-dibromomethane, 100 μL) and vinyldimethylchlorosilane (5.62 g, 46.6 mmol) in 15 mL of THF (the mixture was slightly warmed). After the addition was completed, the reaction mixture was refluxed for 4 hours. Then the mixture was cooled to room temperature, 2 mL of water were added, and the whole was filtered. The organic solvent was evaporated, and the residue was distilled under reduced pressure to afford **12** as a colourless liquid; yield: 4.23 g (81%); bp 66–68 °C/0.6 mmHg. ^{1}H NMR ($CDCl_3$): $\delta = 0.39$ (s, 12H, CH_3), 5.80 (dd, 2H, $J = 3.9$, 20.1 Hz, $SiCH=CH_2$), 6.10 (dd, 2H, $J = 3.9$, 15.0 Hz, $SiCH=CH_2$), 6.34 (dd, 2H, $J = 14.7$, 20.1 Hz, $SiCH=CH_2$), 7.38 (t, 1H, $p-C_6H_4$), 7.58 (d, 1H, $m-C_6H_4$), 7.72 (s, 1H, $SiC-CH-CSi$); ^{13}C NMR ($CDCl_3$): $\delta = -2.74$ (CH_3), 127.02 ($p-C_6H_4$), 132.69 ($SiCH=CH_2$), 134.45 ($m-C_6H_4$), 137.35 ($o-C_6H_4$), 137.88 ($SiCH=CH_2$), 139.02 ($>C-SiCH=CH_2$); ^{29}Si NMR ($CDCl_3$): $d = -10.70$; HR-MS: $m/z = 246.12635$; calcd. for $C_{14}H_{22}Si_2$: 246.12600.

4-(Vinyldimethylsilyl)biphenyl **(13):** A new compound: this vinylsilane was prepared from vinyldimethylchlorosilane and 4-bromobiphenyl according to the synthesis of **12** and obtained by distillation under reduced pressure as a liquid; yield: 95%; bp 79–82 °C/5 mmHg. ^{1}H NMR ($CDCl_3$): $\delta = 0.39$ (s, 6H, CH_3), 5.80 (dd, 1H, $J_{H,H} = 3.9$, 20.1 Hz, $SiCH=CH_2$), 6.09 (dd, 1H, $J_{\mathrm{H,H}} = 3.9$, 20.1 Hz, $\mathrm{SiCH{=}C}\mathit{H}_2$), 6.34 (dd, 1H, $J_{\mathrm{H,H}} = 14.4$, 19.8 Hz, $\mathrm{SiC}\mathit{H}\mathrm{{=}CH_2}$), 7.38 (t, 4H, $m\text{-}\mathrm{C_6}\mathit{H}_4\mathrm{-C_6}\mathit{H}_5$), 7.47 (t, 1H, $\mathrm{-C_6}\mathit{H}_4\text{-}p\text{-}\mathrm{C_6}\mathit{H}_5$), 7.61 (d, 4H, $o\text{-}\mathrm{C_6}\mathit{H}_4\mathrm{-C_6}\mathit{H}_5$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = -2.86$ ($\mathit{C}\mathrm{H_3}$), 126.54 ($m\text{-}\mathit{C}_6\mathrm{H_4}$), 127.10 ($p\text{-}\mathit{C}_6\mathrm{H_5}$), 127.37 ($o\text{-}\mathit{C}_6\mathrm{H_5}$), 128.77 ($m\text{-}\mathit{C}_6\mathrm{H_5}$), 132.77 ($\mathrm{SiCH{=}}\mathit{C}\mathrm{H_2}$), 134.43 ($o\text{-}\mathit{C}_6\mathrm{H_4}$), 137.31 ($>\mathit{C}\mathrm{-}\mathit{C}<$), 141.05 ($\mathrm{Si}\mathit{C}\mathrm{H{=}CH_2}$), 141.79 ($>\mathit{C}\mathrm{-SiCH{=}CH_2}$); ^{29}Si NMR ($\mathrm{CDCl_3}$): $\delta = -11.35$; HR-MS: $m/z = 238.11798$; calcd. for $\mathrm{C_{16}H_{18}Si}$: 238.11778.

***4,4′-Bis(vinyldimethylsilyl)biphenyl* (14):** A new monomer: this compound was prepared from vinyldimethylchlorosilane and 4,4′-dibromobiphenyl according to the synthesis of **12** and obtained by distillation under reduced pressure as a white, crystalline, stable solid; yield: 95%; bp 112–115 °C/0.6 mmHg; mp 42.5–42.9 °C. ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 0.41$ (s, 12H, $\mathrm{C}\mathit{H}_3$), 5.81 (dd, 2H, $J = 3.6$, 20.1 Hz, $\mathrm{SiCH{=}C}\mathit{H}_2$), 6.10 (dd, 2H, $J = 3.9$, 14.7 Hz, $\mathrm{SiCH{=}C}\mathit{H}_2$), 6.34 (dd, 2H, $J = 14.4$, 20.1 Hz, $\mathrm{SiC}\mathit{H}\mathrm{{=}CH_2}$), 7.61 (s, 8H, $o, m\text{-}\mathrm{C_6}\mathit{H}_4\mathrm{-C_6}\mathit{H}_4\mathrm{-}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = -2.76$ ($\mathit{C}\mathrm{H_3}$), 126.46 ($o\text{-}\mathit{C}_6\mathrm{H_4}\mathrm{-}\mathit{C}_6\mathrm{H_4-}$), 132.57 ($\mathrm{SiCH{=}}\mathit{C}\mathrm{H_2}$), 134.36 ($m\text{-}\mathit{C}_6\mathrm{H_4}\mathrm{-}\mathit{C}_6\mathrm{H_4}$), 137.11 ($>\mathrm{C-}\mathit{C}<$), 141.79 ($>\mathit{C}\mathrm{-SiCH{=}CH_2}$), 149.49 ($\mathrm{Si}\mathit{C}\mathrm{H{=}CH_2}$); ^{29}Si NMR ($\mathrm{CDCl_3}$): $\delta = -11.45$; HR-MS: $m/z = 322.15752$; calcd. for $\mathrm{C_{20}H_{26}Si_2}$: 322.15730.

Representative Procedures for Catalytic Reactions

Catalytic tests of silylative homo-coupling reactions: Catalytic screenings were essentially performed under argon using an earlier prepared toluene solution (1 M) of a mixture of vinylphenyldimethylsilane and 1 mol % of ruthenium catalysts at 110 °C for 18 h.

Catalytic tests of silylative cross-coupling reactions: Catalytic screenings were mainly performed under argon using an earlier prepared toluene solution (0.5 M) of a 2 : 1 mixture of vinylphenyldimethylsilane and 1,4-divinylbenzene with 1 mol % of ruthenium catalysts at 80 °C for 18 h.

Procedure of catalytic tests for polycondensation of 1,4-bis(vinyldimethylsilyl)benzene: Catalytic tests were performed in the presence of argon using an earlier prepared toluene solution (1 M) of a mixture of 1,4-bis(vinyldimethylsilyl)benzene and 1 mol % of ruthenium catalysts at 110 °C for 24 h.

General Homopolycondensation Procedure

The syntheses were performed under argon using **7** as a catalyst. Reagents and solvents were dried and deoxygenated. A mixture of **10, 12** or **14** monomer (2.5 mmol), the ruthenium complex **7** (0.025 mmol) and toluene (2.5 mL, 1 M) were placed in a 5-mL mini-reactor. The reaction mixture was stirred and heated at 110 °C under an argon flow for 5–7 days. The isolated yields were between 85 and 92% depending on the combination of starting monomer and derivative of bis(vinyldimethylsilyl)arenes.

General Copolycondensation Procedure

The syntheses processes were carried out under argon, where **7** was used as a catalyst. Reagents and solvents were dried and deoxygenated. A mixture of **10, 12** or **14** monomer (0.78 mmol) with **9** (0.78 mmol), the ruthenium complex **7** (0.0078 mmol) and toluene (1.56 mL, 0.5M) were placed in a 5-mL mini-reactor. The reaction mixture was stirred and heated at 80 °C under an argon flow for 6–7 days. The isolated yields were between 78 and 94% depending on combination of starting monomer and derivative of bis(vinyldimethylsilyl)arenes.

Homopolycondensation Procedure of Monomer 11

***Poly[*p*-phenylene-dimethylsilylene-(*E*)-vinylene]* (15):** A mixture of 0.24 g (1.27 mmol) of **11** and 9.3 mg (0.92×10^{-2} mmol) of complex **7** in 1.27 mL (1 M) of toluene was heated at 80 °C under an argon flow for 7 days. After the reaction was completed, the resulting polymer was isolated and purified by repeated reprecipitation from methanol. Then the final polymeric material was filtered off and dried under vacuum at room temperature to afford homopolymer **15** as a light yellow powder; yield: 0.29 g (88%). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 0.34$ (s, $\mathrm{C}\mathit{H}_3$, external), 0.43 (s, $\mathrm{C}\mathit{H}_3$, internal), 5.26 (d, $J = 10.8$ Hz, $>\mathrm{C-CH{=}C}\mathit{H}_2$, trace), 5.75 (dd, 1H, $J = 3.9$, 19.6 Hz, $\mathrm{SiCH{=}C}\mathit{H}_2$, trace), 5.79 (d, 1H, $J = 17.4$ Hz, $>\mathrm{C-CH{=}C}\mathit{H}_2$, trace), 6.62(d, 1H, $J = 19$ Hz, $>\mathrm{C-}\mathit{H}\mathrm{C{=}CH-Si-}$), 6.78 (dd, 1H, $J = 10.8$, 17.5 Hz, $>\mathrm{C-C}\mathit{H}\mathrm{{=}CH_2}$, trace), 6.93 (s, 1H, $J = 19$ Hz, $>\mathrm{C-HC{=}C}\mathit{H}\mathrm{-Si-}$), 7.44 (d, 2H, $J = 7.8$ Hz, $\mathrm{{=}CH}\text{-}o\text{-}\mathrm{C_6}\mathit{H}_4\mathrm{-}$), 7.53 (d, 2H, $J = 7.8$ Hz, $\mathrm{{=}CH}\text{-}m\text{-}\mathrm{C_6}\mathit{H}_4\mathrm{-}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = -2.50$ ($\mathit{C}\mathrm{H_3}$, external and internal), 114.20 ($>\mathrm{C-HC{=}}\mathit{C}\mathrm{H_2}$, trace), 125.92 ($\mathrm{{=}CH}\text{-}o\text{-}\mathit{C}_6\mathrm{H_4-}$), 127.60 ($>\mathrm{C-H}\mathit{C}\mathrm{{=}CH_2}$), 134.21 ($\mathrm{{=}CH}\text{-}m\text{-}\mathit{C}_6\mathrm{H_4-}$), 138.7 ($>\mathit{C}\mathrm{-HC{=}CH-Si-}$), 138.8 ($\mathrm{-HC{=}CH-Si}\text{-}\mathit{C}<$), 145.32 ($\mathrm{-CH{=}}\mathit{C}\mathrm{H-Si}$); ^{29}Si NMR ($\mathrm{CDCl_3}$): $\delta = -10.52$; FTIR (film): $\nu = 1261$ ($\delta_{\mathrm{sym,\ Si\text{-}Me}}$), 1018 and 987 cm^{-1} ($\gamma_{\mathrm{C-H}}$, *trans*-$\mathrm{C_6H_4}\mathit{HC}\mathrm{{=}}\mathit{CH}\mathrm{Si-}$); anal. calcd. for $\mathrm{(C_{10}H_{12}Si)_n}$: C 74.93, H 7.55; found: C 73.23, H 7.31; TGA: $T_{\mathrm{d10}} = 491$ °C; GPC: $M_w = 18400$, $M_n = 8760$, $M_w/M_n = 2.1$, $n = 55$

Analytical Data of Homopolymers and Copolymers

***Poly[dimethylsilylene-*p*-phenylene-dimethylsilylene-(*E*)-vinylene]* (16):** ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 0.25$ (s, $\mathrm{C}\mathit{H}_3$, external), 0.34 (s, $\mathrm{C}\mathit{H}_3$, internal), 5.75 (dd, 1H, $J = 4$, 24 Hz, $\mathrm{Si-CH{=}C}\mathit{H}_2$, trace), 6.04 (dd, 1H, $J = 4$, 14 Hz, $\mathrm{Si-CH{=}C}\mathit{H}_2$, trace), 6.30 (dd, 1H, $J = 14$, 24 Hz, $\mathrm{Si-C}\mathit{H}\mathrm{{=}CH_2}$, trace), 6.82 (s, 2H, $\mathrm{-SiC}\mathit{H}\mathrm{{=}C}\mathit{H}\mathrm{Si-}$), 7.50 (s, 8H, $\mathrm{-C_6}\mathit{H}_4\mathrm{-}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = -2.71$ ($\mathit{C}\mathrm{H_3}$, internal), -2.6 ($\mathit{C}\mathrm{H_3}$, external), 132.26 ($\mathrm{Si-CH{=}}\mathit{C}\mathrm{H_2}$), 132.87 ($\mathrm{Si}\mathit{C}\mathrm{H{=}CH_2}$), 133.20 ($\mathrm{-}\mathit{C}_6\mathrm{H_4-}$), 139.32 ($>\mathit{C}\mathrm{-Si-}$), 150.22 ($\mathrm{-Si}\mathit{C}\mathrm{H{=}}\mathit{C}\mathrm{H-Si}$); ^{29}Si NMR ($\mathrm{CDCl_3}$): $\delta = -11.78$; FT-IR (film): $n = 1250$ ($\delta_{\mathrm{Si\text{-}Me}}$), 1008 cm^{-1} ($\gamma_{\mathrm{C-H}}$, *trans*-$\mathrm{Si}\mathit{HC}\mathrm{{=}}\mathit{CH}\mathrm{Si-}$); anal. calcd. for $\mathrm{(C_{12}H_{18}Si_2)_n}$: C 65.98, H 8.31; found: C 65.76, H 8.41; TGA: $T_{\mathrm{d10}} = 447$ °C; GPC: $M_w = 16300$, $M_n = 10190$, $M_w/M_n = 1.6$, $n = 47$. The compound was isolated as a white powder.

***Poly[dimethylsilylene-*m*-phenylene-dimethylsilylene-(*E*)-vinylene]* (17):** ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 0.34$ (s, $\mathrm{C}\mathit{H}_3$, external), 0.35 (s, $\mathrm{C}\mathit{H}_3$, internal), 5.78 (dd, 1H, $J = 4$, 24 Hz, $\mathrm{SiCH{=}C}\mathit{H}_2$, trace), 6.06 (dd, 1H, $J = 4$, 14 Hz, $\mathrm{SiCH{=}C}\mathit{H}_2$, trace), 6.32 (dd, 1H, $J = 14$, 24 Hz, $\mathrm{SiC}\mathit{H}\mathrm{{=}CH_2}$, trace), 6.84 (s, $\mathrm{SiC}\mathit{H}\mathrm{{=}C}\mathit{H}\mathrm{Si}$), 7.31–7.36 (m, $m\text{-}\mathrm{C_6}\mathit{H}_4\mathrm{-}$), 7.50 (d, $o\text{-}\mathrm{C_6}\mathit{H}_4\mathrm{-}$), 7.67 (s, $\mathrm{SiC-C}\mathit{H}\mathrm{-CSi}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = -2.72$ ($\mathit{C}\mathrm{H_3}$, internal), -2.66 ($\mathit{C}\mathrm{H_3}$, internal), 127.03 ($p\text{-}\mathit{C}_6\mathrm{H_4}$), 134.50 ($m\text{-}\mathit{C}_6\mathrm{H_4}$), 137.50 ($\mathrm{Si-C-}\mathit{C}\mathrm{H-C-Si}$), 139.15 ($>\mathit{C}\mathrm{-Si}$-

HC=CH–), 150.23 (–Si*C*H=*C*HSi–); ^{29}Si NMR ($CDCl_3$): $\delta = -11.49$; FT-IR (film): $\nu = 1260$ ($\delta_{sym,\ Si\text{-}Me}$), 1009 cm^{-1} ($\gamma_{C\text{–}H}$, *trans*–Si*HC*=*CH*Si); anal. calcd. for $(C_{12}H_{18}Si_2)_n$: C 65.98, H 8.31; found: C 65.76, H 8.21; TGA: $T_{d10} = 433\,°C$; GPC: $M_w = 16400$, $M_n = 9650$, $M_w/M_n = 1.7$, $n = 44$. The compound was isolated as a white powder.

***Poly[dimethylsilylene*-p-*biphenylene-dimethylsilylene-(*E*)-vinylene]* (18):** ^1H NMR ($CDCl_3$): $\delta = 0.38$ (s, C*H*$_3$, internal), 6.88 (s, 2H, Si*HC*=*CH*Si), 7.60 (s, 8H, –C$_6$*H*$_4$–C$_6$*H*$_4$–); ^{13}C NMR ($CDCl_3$): $\delta = -2.70$ (*C*H$_3$, internal), 126.45 (*o*-*C*$_6$H$_4$–*C*$_6$H$_4$–), 134.29 (*m*-*C*$_6$H$_4$–*C*$_6$H$_4$–), 137.31 (>*C*–*C*<), 141.53 (>*C*–SiHC=CH–), 150.22 (–Si*C*H=*C*HSi); ^{29}Si NMR ($CDCl_3$): $\delta = -11.43$; FT-IR (film): $\nu = 1262$ ($\delta_{sym,\ Si\text{-}Me}$), 990 cm^{-1} ($\gamma_{C\text{–}H}$, *trans*-Si*HC*=*CH*Si–); anal. calcd. for $(C_{18}H_{22}Si_2)_n$: C 73.40, H 7.53; found: C 73.15, H 7.39; TGA: $T_{d10} = 486\,°C$; GPC: $M_w = 34800$, $M_n = 13290$, $M_w/M_n = 2.5$, $n = 47$. The compound was isolated as a white powder.

***Poly[dimethylsilylene*-p-*phenylene-dimethylsilylene-(*E*)-vinylene*-p-*phenylene-(*E*)-vinylene]* (19):** ^1H NMR ($CDCl_3$): $\delta = 0.33$ (s, 12H, C*H*$_3$, external), 0.41 (s, 12H, C*H*$_3$, internal), 5.75 (dd, $J = 4$, 24 Hz, SiCH=C*H*$_2$, trace), 6.04 (dd, $J = 4$, 15 Hz, Si–CH=C*H*$_2$, trace), 6.27(dd, $J = 15$, 20 Hz, >C–*H*C=CH–Si-, trace), 6.56 (d, 1H, $J = 19$ Hz, >C–C*H*=CH–Si–), 6.92 (d, 1H, $J = 19$ Hz, >C–HC=C*H*–Si–), 7.36 (s, 4H, –C$_6$*H*$_4$–), 7.56 (s, 4H, –Si–C$_6$*H*$_4$–Si–); ^{13}C NMR ($CDCl_3$): $\delta = -2.9$ (*C*H$_3$, external), -2.60 (*C*H$_3$, internal), 114.10 (>C–HC=*C*H$_2$, trace), 126.69 (–*C*$_6$H$_4$–), 127.16 (>C–H*C*=CH–Si), 132.89 (–Si-HC=*C*H$_2$), 133.26 (Si-*C*$_6$H$_4$–Si), 137.91 (>*C*–HC=CH–Si–), 139.41 (–HC=CH–Si-*C*<), 144.78 (–CH=*C*H–Si–); ^{29}Si NMR ($CDCl_3$): $\delta = -10.35$; FT-IR (film): $\nu = 1248$ ($\delta_{sym,\ Si\text{-}Me}$), 985 cm^{-1} ($\gamma_{C\text{–}H}$, *trans*-C$_6H_4$*HC*=*CH*Si–); anal. calcd. for $(C_{20}H_{24}Si_2)_n$: C 74.93, H 7.55; Found: C 74.31, H 7.38; TGA: $T_{d10} = 464\,°C$; GPC: $M_w = 17600$, $M_n = 8800$, $M_w/M_n = 2.0$, $n = 28$. The compound was isolated as a light yellow powder.

***Poly[dimethylsilylene*-m-*phenylene-dimethylsilylene-(*E*)-vinylene*-p-*phenylene-(E)-vinylene]* (20):** ^1H NMR ($CDCl_3$): $\delta = 0.33$ (s, 12H, C*H*$_3$, external), 0.43 (s, C*H*$_3$, internal), 6.60 (d, 1H, $J = 19.2$ Hz, >C–*H*C=CH–Si), 6.93 (d, 1H, $J = 19.2$ Hz, >C–HC=C*H*–Si–), 7.21 (s, 4H, –C$_6$*H*$_4$–), 7.36–7.39 (m, *m*-C$_6$*H*$_4$–), 7.60 (d, *o*–C$_6$*H*$_4$–), 7.77 (s, SiC–C*H*–CSi); ^{13}C NMR ($CDCl_3$): $\delta = -2.88$ (*C*H$_3$, external), -2.52 (*C*H$_3$, internal), 126.73 (–*C*$_6$H$_4$–), 127.24 (*m*-*C*$_6$H$_4$–), 127.46 (>C–H*C*=CH–Si), 134.79 (*o*-*C*$_6$H$_4$–), 137.72 (>*C*–HC=CH–Si–), 138.04 (SiC–*C*H–CSi–), 139.24 (–HC=CH–Si-*C*<), 144.82 (–CH=*C*H–Si–); ^{29}Si NMR ($CDCl_3$): $\delta = -10.09$; FT-IR (film): $\nu = 1250$ ($\delta_{sym,\ Si\text{-}Me}$), 988 cm^{-1} ($\gamma_{C\text{–}H}$, *trans*-C$_6H_4$*HC*=*CH*Si–); anal. calcd. for $(C_{20}H_{24}Si_2)_n$: C 74.93, H 7.55; found: C 74.33, H 7.37; TGA: $T_{d10} = 473\,°C$. GPC: $M_w = 13100$, $M_n = 5960$, $M_w/M_n = 2.2$, $n = 18$. The compound was isolated as a light brown powder.

***Poly[dimethylsilylene*-p-*biphenylene-dimethylsilylene-(*E*)-vinylene*-p-*phenylene-(*E*)-vinylene]* (21):** ^1H NMR ($CDCl_3$): $\delta = 0.47$ (s, 12H, C*H*$_3$, internal), 6.62 (d, 1H, $J = 19.2$ Hz, >C–*H*C=CH–Si), 6.96 (d, 1H, $J = 19.2$ Hz, >C–HC=C*H*–Si–), 7.43 (s, 4H, –C$_6$*H*$_4$–), 7.59–7.67 (m, –C$_6$*H*$_4$–C$_6$*H*$_4$–); ^{13}C NMR ($CDCl_3$): $\delta = -2.35$ (*C*H$_3$, internal), 126.50 (*m*–*C*$_6$H$_4$–*C*$_6$H$_4$–), 126.65 (–*C*$_6$H$_4$–), 127.14 (>C–H*C*=CH–Si), 134.32 (*o*–*C*$_6$H$_4$–*C*$_6$H$_4$–), 137.31 (>*C*–*C*<), 137.84 (>*C*–HC=CH–Si), 141.61 (–HC=CH–Si-*C*<), 144.74 (–CH=*C*H–Si–); ^{29}Si NMR ($CDCl_3$): $\delta = -10.02$; FT-IR (film): $\nu = 1259$ ($\delta_{sym,\ Si\text{-}Me}$), 992 cm^{-1} ($\gamma_{C\text{–}H}$, *trans*-C$_6H_4$*HC*=*CH*Si–); anal. calcd. for $(C_{26}H_{28}Si_2)_n$: C 78.72, H 7.11; found: C 77.98, H 7.05; TGA: $T_{d10} = 478\,°C$; GPC: $M_w = 24600$, $M_n = 8480$, $M_w/M_n = 2.9$, $n = 21$. The compound was isolated as a white powder.

The progress of the synthesis reactions of homopolymers and copolymers, in the initial stage, was monitored by GC-MS and ^1H NMR. The isomer structures were confirmed by DEPT analysis. The polymeric materials were isolated according to the work-up of procedure **15**. The polymers were soluble in some organic solvents, such as chloroform, CH_2Cl_2 and THF, but insoluble in benzene, toluene and alcohols, that is why the polymers were readily separated from the reaction mixture by reprecipitation from alcohols.

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