Dramatic Increase in Thermal Stability by Partial Phenylethynylation at the Silicon Center in Poly[(dihydrosilylene)-1,3-phenylene]

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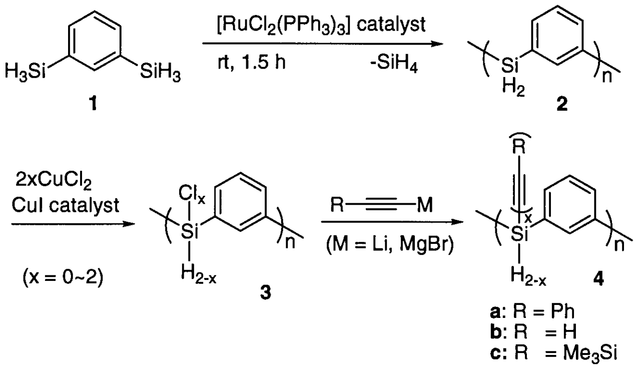
Partial ethynylation of the Si-H in poly[(dihydrosilylene)(1,3-phenylene)] dramatically increases thermal stability of the polymer. The T_{d5} value observed for $[SiH_{1.44}(C{\equiv}CPh)_{0.56}(1,3\text{-}C_6H_4)]_n$ is 820 °C, which is much higher than the value (586 °C) of a commercial polyimide (Kapton, DuPont).

Synthesis and derivatization of organosilicon polymers are increasingly important because the polymers are promising functional materials such as semiconductors[1] and ceramic precursors.[2] One of the authors has reported that the dehydrogenative coupling polymerization reaction proceeds between phenylsilane and 1,3-diethynylbenzene in the presence of magnesium oxide or barium alkoxide used as catalyst. The resulting polymer, MSP, comprising -Si(H)Ph-C≡C-1,3-C_6H_4-C≡C- repeat units, possesses an extremely high thermal stability.[3] The presence of Si-H and -C≡C- moieties appears to play a crucial role to display the high stability. However, MSP has both Si-H and -C≡C- moieties in the backbone of the polymer and its structure cannot be widely modified for better tuning of the thermal and mechanical properties. On the other hand, we have reported the desilanative polycondensation of 1,3-disilylbenzene (**1**) using ruthenium-phosphine complex catalysts, which affords poly[(dihydrosilylene)(1,3-phenylene)] (**2**) (Scheme 1).[4,5] The principal advantage of poly[(dihydro-silylene)(phenylene)]s lies in their versatile reactivity for the structural modification; we have already demonstrated this merit by transforming the Si-H into Si-OR by the reaction with phenol (R = C_6H_5) or methanol (R = CH_3) in the presence of the ruthenium complex catalyst. Another example is the treatment of **2** with air, which gave a highly heat-resistant polymer.[4] In this paper we disclose partial ethynylation of **2** affords soluble and extremely thermally stable polymers.



Scheme 1.

Derivatization of the polymers are summarized in Scheme 1. In a typical procedure, a solution of **2** (54 mg, 0.5 mmol in terms of the repeat unit) in 2 ml of freshly distilled THF was added to $CuCl_2$ (137 mg, 1.0 mmol) and CuI (5 mg, 0.026 mmol) as catalyst.[6] The mixture was stirred at room temperature for 15 min and was filtered. Evaporation gave spectroscopically pure poly[(chlorosilylene)(1,3-phenylene)] (**3**) in a nearly quantitative yield, which displayed a ^{29}Si NMR signal at -5.45 ppm (J_{SiH} = 240 Hz). Treatment of a dry THF (1.5 ml) solution of **3** (68 mg, 0.5 mmol in terms of the repeat unit) with a phenylethynyllithium solution (1 M in THF, 0.5 ml) over 15 min, evaporation, and addition of toluene (3 ml) led to the separation of LiCl. Filtration and evaporation of the filtrate afforded a polymeric material, which was subjected to preparative GPC. A fraction of *Mw* range of 30000-18000 was collected (52%) to give poly[{(phenylethynyl)silylene}(1,3-phenylene)] (**4aV**) as yellow solid.[7] Similar treatments of **3** with ethynylmagnesium bromide and trimethylsilylethynyllithium respectively gave poly[(ethynylsilylene)(1,3-phenylene)] (**4b**, brown solid) and poly[{(trimethylsilylethynyl)silylene)}(1,3-phenylene)] (**4c**, reddish brown solid).[8] These polymers were stable towards moist air and were soluble in THF, benzene, and toluene, but not in hexane and methanol.

Use of less than two equivalents of $CuCl_2$ (relative to a SiH_2 unit) in the chlorination of **2** gave partially mono-chlorinated polymers as colorless liquid. Subsequent reactions of these polymers with equimolar amounts of phenylethynyllithium (relative to the chlorine content) gave partially phenylethynylated polymers, $[\{SiH_{2-x}(C{\equiv}CC_6H_5)_x\}(1,3\text{-}C_6H_4)]_n$ [x = 0.16 (**4aI**), 0.56 (**4aII**), 0.69 (**4aIII**), 0.88 (**4aIV**)]. Polymers (**4aI-IV**) isolated by preparative GPC were pale yellow solids, which displayed satisfactory NMR and IR spectroscopic data. The content of the phenylethynyl moiety determined by the integration of the SiH and SiH_2 signals in ^{1}H NMR spectroscopy was in good agreement with the value expected for the amount of $CuCl_2$ used in the chlorination of **2**. These polymers were also soluble in benzene, toluene, and THF. Softening temperatures of **4aI-V** ranged from 75 to 100 °C. A similar procedure using four equivalents of $CuCl_2$ provided bisphenylethynyl polymer (**5**) as brown crystalline solid.[9]

Profiles of thermogravimetric analyses (TGA) of **2**, **4aI-V**, **4b**, **4c** and **5**, are illustrated in Figure 1 and temperatures of 5% weight loss (T_{d5}) and char yields at 1000 °C in N_2 atmosphere determined by TGA are summarized in Table 1. Comparison of TGA profiles and the data in Table 1 shows that polymers **4aV**, **4b** and **4c** possess higher T_{d5} values than **2** and that the thermal stability of the polymer depending on the R group in the C≡CR substituent decreases in the order R: Ph > H > $SiMe_3$. Very interestingly, partially mono-phenylethynylated polymers prepared to explore higher thermal stabilities indeed displayed dramatically increased T_{d5} values, albeit very much dependent on the extent of the substitution. Thus the value increased from

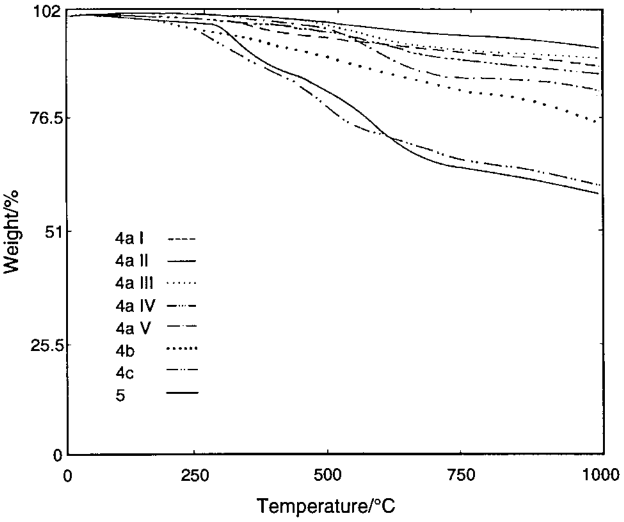


Figure 1. TGA profile of $[SiH_{2-x}(C{\equiv}CR)_x\text{-}1,3\text{-}C_6H_4]_n$ under N_2 at 10 °C/min.

Table 1. Molecular weight and thermal property of $[SiH_{2-x}(C{\equiv}CR)_x\text{-}1,3\text{-}C_6H_4]_n{}^a$

R	Polymer	x	$M_w/M_n{}^b$	Yield /%	$T_{d5}{}^c$ /°C	Char at 1000 °C/%
Ph	**2**	0	10400/7300	80	197 (337)	74
	4aI	0.16	27200/11800	65	500	89
	4aII	0.56	23000/6800	60	820 (546)	94
	4aIII	0.69	15300/9200	57	577	92
	4aIV	0.88	21000/7900	53	569 (452)	91
	4aV	1	25800/8700	52	523	84
	5	2	13000/3400	36	291	62
H	**4b**	1	9000/3100	61	325	75
$SiMe_3$	**4c**	1	15900/7700	47	245	64

[a] Yields and M_w/M_n are values for isolated polymers after preparative GPC. [b] The diversity in the molecular weight is due not only to the difference in x (extent of substitution), but also to the difference in the molecular weight of the starting **2**, which was prepared each time prior to the substitution reaction. [c] Temperatures in parentheses are T_{d5} values under air.

197 °C for the unsubstituted one (**2**) to 500 °C upon 16% mono-phenylethynylation (**4aI**), and further to 820 °C upon 56% mono-phenylethynylation (**4aII**). Thereafter the T_{d5} values started declining to display 577, 569, and 523 °C for 69% (**4aIII**), 88% (**4aIV**), and 100% (**4aV**) mono-substitutions respectively. The T_{d5} value of the exhaustively disubstituted one (x = 2), polymer **5**, was even lower to display only 291 °C. This tendency was demonstrated notwithstanding the diversity of the molecular weight. These results clearly suggest that the coexistence of SiH and Si(C≡CPh) units is essential to achieve the high thermal stability. Among phenylethynylated polymers in particular, the presence of SiH_2 and SiH(C≡CPh) units in a 1 : 1 ratio appears to be most beneficial to the thermal stability. As proposed for MSP,[3] the thermal stability of the present polymer is due presumably to the cross-linking between the SiH_2 and C≡CPh units by the hydrosilation reaction. T_{d5} values of **4aII** under N_2 (820 °C) and under air (546 °C, which is higher than those of **2** and **4aIV**) are comparable to those of MSP (860 °C and 567 °C, respectively).[3b]

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7 **4aV**: ^{29}Si NMR (C_6D_6) δ -39.68 (J_{SiH} = 214 Hz); ^{1}H NMR (C_6D_6) δ 5.55 (s, 1H, SiH); ^{13}C NMR (C_6D_6) δ 87.62, 110.69 (C≡C), 122.80, 125.66, 128.47, 129.16, 132.50, 132.90, 137.47, 142.65 (aromatic).

8 **4b**: ^{29}Si NMR (C_6D_6) δ -39.78 (J_{SiH} = 216 Hz); ^{1}H NMR (C_6D_6) δ 2.14 (s, 1H, CH), 5.29 (s, 1H, SiH); ^{13}C NMR (C_6D_6) δ 83.13, 99.00 (C≡C), 127.87, 131.63, 137.40, 142.30 (aromatic). Ethynyldiphenyl-silane: ^{29}Si NMR (C_6D_6) δ -39.97 (J_{SiH} = 215 Hz); ^{1}H NMR (C_6D_6) δ 2.18 (s, 1H, CH), 5.37 (s, 1H, SiH); ^{13}C NMR (C_6D_6) δ 83.13, 99.00 (C≡C), 128.57, 130.59, 131.76, 135.59 (aromatic). **4c**: ^{29}Si NMR (C_6D_6) δ -17.62 (s, $SiMe_3$), -40.99 (J_{SiH} = 214 Hz, SiH); ^{1}H NMR (C_6D_6) δ 5.29 (s, 1H, SiH); ^{13}C NMR (C_6D_6) δ 106.70, 120.47 (C≡C), 128.54, 132.04, 137.35, 142.56 (aromatic). (Trimethylsilylethynyl)-diphenylsilane: ^{29}Si NMR (C_6D_6) δ -17.69 (s, $SiMe_3$), -41.14 (J_{SiH} = 212 Hz, SiH); ^{1}H NMR (C_6D_6) δ 5.45 (s, 1H, SiH); ^{13}C NMR (C_6D_6) δ 107.05, 119.95 (C≡C), 128.49, 130.42, 132.21, 135.57 (aromatic).

9 **5**: ^{29}Si NMR (C_6D_6) δ -47.05; ^{13}C NMR (C_6D_6) δ 88.37, 109.93 (C≡C), 122.20, 126.30, 128.61, 129.26, 132.65, 132.75, 137.52, 142.25 (aromatic). Bis(phenylethynyl)-diphenylsilane: ^{29}Si NMR (C_6D_6) δ -47.07; ^{13}C NMR (C_6D_6) δ 88.58, 109.60 (C≡C), 122.71, 128.59, 128.67, 129.49, 130.79, 132.61, 133.49, 135.48 (aromatic).