relative SH intensity remained almost unchanged for several days after poling and then gradually decreased over a period of a few months, and d_{33} reached a level of about 60–70% of the initial value and d_{33} = 18 pm/V at 2500 h (3.5 months) after poling and stayed constant after that, to the end of our observation at 3600 h (5 months). This value is considered very high compared with other polymers previously reported, although temporal decay of only a short period has been reported (ca. 70% after 800 h,[2] ca. 60% after 120 h,[4] and ca. 70% after 670 h[12]). The slow temporal decay of this polymer may be attributed to the short spacer group between the polymer and the chromophore unit. The propagation loss of this film was determined to be about 10 dB/cm at 632.8 nm for the prism coupling intensity of a waveguide using He–Ne laser beam.

In conclusion, MNPAMS, the vinyl monomer having a pNA unit, provided glassy polymers transparent in the wavelength region longer than 480 nm. Although the order parameter of this poled polymer was low, high *d* coefficients and slow temporal decay were obtained by high chromophore concentration and a short spacer.

Registry No. MNPAMS (homopolymer), 130525-38-1; $H_2C{=}CHC_6H_4$-*p*-CH_2Cl, 1592-20-7; $H_3CNHC_6H_4$-*p*-NO_2, 100-15-2; MNPAMS, 130525-37-0.

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Selective Synthetic Routes to Electroconductive Organosilicon Polymers Containing Thiophene Units

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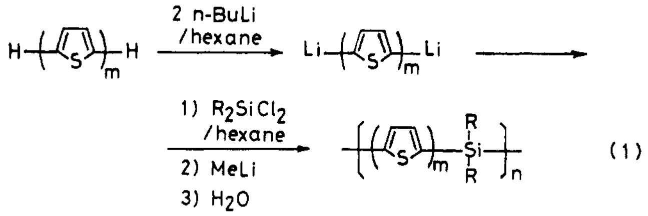
Our current interest in organosilicon polymeric materials containing alkyne diyl segments[1] led us to investigate the preparation of other new unsaturated polymers containing silylene and thienylene units. Polythiophene, prepared by electrochemical[2,3] or chemical[4] methods, and related polyheterocyclic polymers[5] constitute an important class of organic electroconductive materials. The properties can be tuned by varying the molecular composition of the polymer.[6] Various studies have been performed in modifying the chain unit[7,8] and preparing copolymers,[9] and composites[10] in order to assess the molecular properties for various uses and to study the rules governing transport properties in these polymeric materials.

We were interested in investigating the introduction of silicon atoms into the polymer chain. Polymers with alternating silylene and thienylene units would be of interest in terms of properties based on a structure capable of dπ–pπ conjugation.[11] Delocalization of the π-electron density along the main chain can lead to an electroactive material by oxidative doping. Interestingly, related carbon-bridged thiophene polymer precursors to multiblock conjugated copolymers exhibiting semiconductivity and third-order nonlinear optical properties have been recently described.[12] Moreover, the introduction of a silicon atom along the polymer chain can allow attachement of a variety of functional groups. Functionalized poly(thiophenes) with original properties have been recently described.[13] Also, owing to the photochemical reactivity of polysilane units,[14,15] related polymers might be of interest for photolithographic applications.[16] In connection to this, a poly[2,5-bis(dimethylsilyl)thiophene] with high thermal stability was recently reported to undergo degradation upon photolysis.[17]

We report here the synthesis of molecularly defined poly[2,5-silylthiophene] with one to five thienylene and up to six silylene units in the polymer chain. Our objective was to prepare a variety of polymers with alternating thienylene and silylene units that can be used as models for conductivity studies. To achieve a selective synthesis of the various desirable chain units, two methods have been used: (i) We first studied the coupling reactions of dilithio derivatives of mono-, di-, and terthiophene with chlorosilanes (eq 1).



(1)

The lithiation was achieved in hexane, and the condensation was carried out by slow addition of the required

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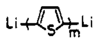
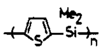
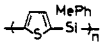
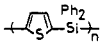
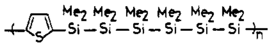
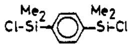
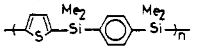
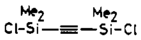
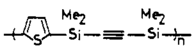
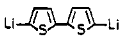
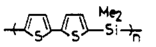
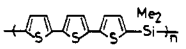
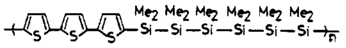
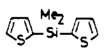
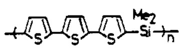
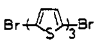
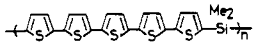
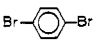
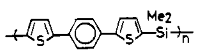
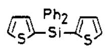
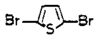
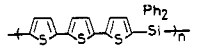
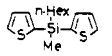
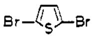
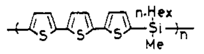
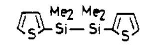
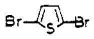
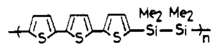
Table I. Reactions of Dilithiophene Derivatives with Chlorosilanes[a] (Eq 1)

[b]	dichlorosilane	reaction product	yield	M_w[c]	M_w/M_n	$\bar{n}$	mp,[d] °C	conductivity,[e] S cm^{-1}
	Me_2SiCl_2		60	5940	1.4	30	130–132	
	$PhMeSiCl_2$		51	3169	1.9	8	70–77	
	Ph_2SiCl_2		76				235–239	
	$Cl\text{-}(SiMe_2)_6\text{-}Cl$		54	3900	1.8	5	135–137	
			75	4760	1.7	10	184–186	10^{-3}–10^{-4}
			90	2550	1.2	10	103–112	
	Me_2SiCl_2		80	2550	1.2	9	184–186	3 × 10^{-5}
	Me_2SiCl_2		67	3760	1.4	8	191–193	10^{-1}
	$Cl\text{-}(SiMe_2)_6\text{-}Cl$		79	6460	1.5	7	>350	

[a] The reaction was carried out by slow addition of the required dichlorosilane to a hexane solution of dilithiophene derivative from 0 °C to room temperature. The mixture was then heated at 50 °C for 1 h and treated with 0.2 mol equiv of MeLi to achieve methylation of the unreacted Si–Cl bonds before hydrolytic workup. The products were purified by dissolution in THF and precipitation with methanol. [b] Dilithiation of bi- and terthiophene was performed as described in the case of thiophene.[17] [c] The molecular weights were determined by using GPC analysis, and the results are relative to polystyrene standards. [d] Sharp melting points were observed by using a Gallenkamp melting point apparatus. [e] Conductivity values have been determined on thin films of polymers cast on glass substrate, by the use of the four-probe point technique.

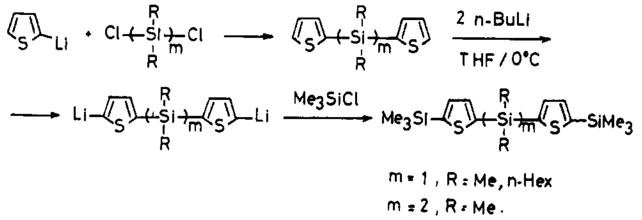
Table II. Reactions of Dimetalated Bis(thienyl)silane with Aryl Dibromide[a] (Eq 3)

bis(thienyl)-silane	aryl dibromide	reaction product	yield, %	M_w[b]	M_w/M_n	$\bar{n}$	mp, °C	conductivity,[d] S cm^{-1}
			66	2230	1.3	6	170–174	2 × 10^{-2}
			70	2350	1.2	4	260–290	4.1 × 10^{-2}
			52	1590	1.2	4	190–210	<10^{-6}
			70	2510	1.5	5	oil	4 × 10^{-2}
			95	1930	1.3	4	oil	1.2 × 10^{-2}
			77	5440	1.3	11	178–184	7 × 10^{-2}

[a] The dilithiation of the bis(thienyl)silane was carried out at 0 °C for 3 h in THF. The zinc derivative was obtained by addition of dry $ZnCl_2$ and additional stirring for 1 h at 0 °C. The zinc reagent was then added to a solution of the required aryl dibromide in THF with 1 mol % of $(PPh_3)_4Pd$. The mixture was then stirred for 20 h at 50 °C, and the product isolated after hydrolytic workup and precipitation. [b] See footnote *c* in Table I. [c] See footnote *d* in Table I. [d] See footnote *e* in Table I.

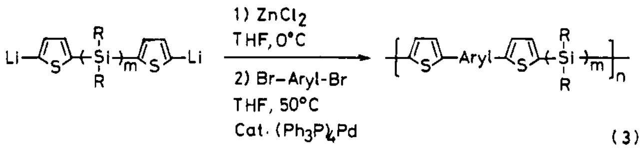
dichlorosilane as indicated in Table I. Treatment with methyllithium allowed methylation of the Si–Cl chain termination. Molecular weights in the range M_w = 2500–6500 relative to polystyrene standards were determined. The polymers were characterized by using IR and liquid or solid NMR spectroscopy. The ^1H, ^{13}C, and ^{29}Si NMR spectra of all compounds are consistent with the assigned structure of the polymer chain and with the presence of thienyl and trimethylsilyl end groups. Various poly(silylthiophenes) with one to three thienylene and one or six dimethylsilylene groups in the chain unit have been obtained (Table I).

(ii) We then examined the metal-catalyzed coupling reaction with aromatic dihalides[18] to form polyaromatic linkages. Dithienylsilane derivatives were first prepared upon reaction of thienyllithium with chlorosilanes and showed to undergo quantitative and regioselective metalation upon treatment with butyllithium at 0 °C in THF (eq 2). The polycondensation reaction with aromatic



(2)

dibromides was then achieved by using the palladium-catalyzed coupling of zinc derivatives[18] as shown in eq 3.



(3)

The results are presented in Table II. Upon reaction of 2,5-dibromothiophene, chain units containing three or five thienylene and one or two silyene groups were obtained.

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(18) Corriu, R. J. P.; Masse, J. P. *J. Chem. Soc., Chem. Commun.* **1972**, 144. Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374. Cunningham, D. D.; Laguren-Davidson, L.; Mark, H. B.; Pham, C. V.; Zimmer, H. *J. Chem. Soc., Chem. Commun.* **1987**, 1021.

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Molecular weights in the range M_w = 2000–5500 were measured. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of all compounds are in agreement with the assigned structure and allowed detection thienyl and bromothienyl chain terminations.

Therefore, by using the polycondensation reaction of dilithiothiophene derivatives with chlorosilanes or arylbromides, we have been able to prepare a variety of polymers with alternating silylene and thienylene units. The thienylene groups are unequivocally linked 2.5 throughout, and the order and stoichiometry of the units is completely defined with no branching nor cross-linking. Some of these polymers have been cast to thin films by spin coating from their solutions leading to insulating films. Under addition of an electron acceptor, such as $NOBF_4$ in CH_2Cl_2 solution, these polymers turned black due to their doping by the BF_4^- anion. These doped polymers have been cast as thin films on a glass substrate, and the conductivity of these films has been determined by the four-point probe technique. The results are given in Tables I and II. In their indoped state, these organosilicon polymers are insulators. Upon doping with $NOBF_4$, the conductivity reaches 10^{-2}–10^{-1} S cm^{-1}, characteristic of a conducting state. These relatively high conductivity values are comparable to those obtained with fully conjugated organic polymers.[2-5] Recent work on polyyne polymers has shown that intercalation of silicon atoms in a conjugated polymeric carbon blackbone still allows the charges to be transfered.[1,20] Our results indicate that the conductivity value increases with the number of consecutive thienylene units in the chain. Three consecutive thienylenes are necessary to reach the range 10^{-2}–10^{-1} S cm^{-1}. However the conductivity values or the polymers with five and three thienylene units are essentially the same. Comparatively little change is introduced by the substitution at silicon or when two consecutive silicon atoms are present. The introduction of phenyl substituents here does not result in an increase in conductivity as observed for silyl polyynes.[1] The increase of the conjugation length in the polymer segment between two silicon atoms has a determining effect on the electrical conductivity of the polymer. When compared to a polymer containing one thiophene between two silicon, the polymers with a longer planar terthiophene unit might allow a better packing of the macromolecules facilitating the charge propagation. This result can be explained also by considering the models recently proposed for the interpretation of the charge-transport properties of conjugated polymers.[21] As a matter of fact, the interchain hopping of the charge, which is the determining step for charge propagation, is very sensitive to the length of the conjugated chains, as observed here. Thus, in turn, it appears possible to modulate the charge-transport properties by appropriate modification of the chain units. In this respect, poly(silylthiophene) appears to be a promising class of polymers. Moreover one can envisage introduction of various substitution functionalities at silicon that should allow additional tuning of the properties.

Registry No. $(Me_2SiCl_2)(Li(C_4H_2S)Li)$ (copolymer), 130904-44-8; $(Me_2SiCl_2)(Li(C_4H_2S)Li)$ (SRU), 130904-62-0; $(PhMeSiCl_2)(Li(C_4H_2S)Li)$ (copolymer), 130904-45-9; $(PhMeSiCl_2)(Li(C_4H_2S)Li)$ (SRU), 130904-63-1; $(Ph_2SiCl_2)(Li(C_4H_2S)Li)$ (copolymer), 130904-46-0; $(Ph_2SiCl_2)(Li(C_4H_2S)Li)$ (SRU), 130904-64-2; $(Cl(SiMe_2)Cl)(Li(C_4H_2S)Li)$ (copolymer), 130904-47-1; $(Cl(SiMe_2)Cl)(Li(C_4H_2S)Li)$ (SRU), 130932-82-0; $(ClSiMe_2C_6H_4\text{-}p\text{-}SiMe_2Cl)(Li(C_4H_2S)Li)$ (copolymer), 130904-48-2; $(ClSiMe_2C_6H_4\text{-}p\text{-}SiMe_2Cl)(Li(C_4H_2S)Li)$ (SRU), 130904-65-3; $(ClSiMe_2C{\equiv}CSiMe_2Cl)(Li(C_4H_2S)Li)$ (copolymer), 130904-49-3; $(ClSiMe_2C{\equiv}CSiMe_2Cl)(Li(C_4H_2S)Li)$ (SRU), 130904-66-4; $(Me_2SiCl_2)(Li(C_4H_2S)_2Li)$ (copolymer), 130904-51-7; $(Me_2SiCl_2)(Li(C_4H_2S)_2Li)$ (SRU), 130904-67-5; $(Me_2SiCl_2)(Li(C_4H_2S)_3Li)$ (copolymer), 130904-53-9; $(Me_2SiCl_2)(Li(C_4H_2S)_3Li)$ (SRU), 130904-68-6; $(Cl(SiMe_2)_6Cl)(Li(C_4H_2S)_3Li)$ (copolymer), 130904-54-0; $(Cl(SiMe_2)_6Cl)(Li(C_4H_2S)_3Li)$ (SRU), 130904-69-7; (bis(thienyl)silane)(dibromothiophene) (copolymer), 130904-55-1; (bis(thienyl)silane)(dibromotrithiophene) (copolymer), 130904-56-2; (bis(thienyl)silane)(dibromotrithiophene) (SRU), 130904-70-0; (bis(thienyl)silane)(dibromobenzene) (copolymer), 130904-57-3; (bis(thienyl)silane)(dibromobenzene) (SRU), 130904-71-1; (bis(thienyl)diphenylsilane)(dibromothiophene) (copolymer), 130904-58-4; (bis(thienyl)diphenylsilane)(dibromothiophene) (SRU), 130904-72-2; (bis(thienyl)-*n*-hexylmethylsilane)(dibromothiophene) (copolymer), 130904-60-8; (bis(thienyl)-*n*-hexylmethylsilane)(dibromothiophene) (SRU), 130904-73-3; (bis(thienyl)dimethylsilane)(dibromothiophene) (copolymer), 130904-61-9; (bis(thienyl)dimethylsilane)(dibromothiophene) (SRU), 130932-83-1.

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Polymer-Precursor Routes to Metal Borides: Syntheses of TiB_2 and ZrB_2

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Boron forms binary compounds with most metals, and these materials are in general high-melting, extremely hard solids with high degrees of thermal stability and chemical inertness. In addition, many metal borides also have metallike conductivity and/or unusual magnetic properties. As a result, these materials have numerous possible structural and electronic applications.[1] Many of these applications will, however, require the development of new processable chemical or polymeric precursors in order to obtain these borides in film, coating, fiber, or shaped material forms. In this communication we report the high-yield syntheses of two metal borides, TiB_2 and ZrB_2, by means of a potentially general synthetic approach that may prove to be useful for the production of a wide range of metal borides in processed forms.

Metal borides have classically been made by a number of different high-temperature powder techniques, with one of the most common methods being the reduction of the metal oxide with boron carbide and carbon:[1]

$$MO_2 + \tfrac{1}{2}B_4C + \tfrac{3}{2}C \rightarrow MB_2 + 2CO \qquad (1)$$

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