Molecular weights in the range $M_w = 2000\text{–}5500$ were measured. ^1H, ^{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 $10^{-2}\text{–}10^{-1}$ 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 $10^{-2}\text{–}10^{-1}$ 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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(20) Oshshita, J.; Furumor, K.; Ishikawa, M.; *Organometallics* **1989**, *8*, 2084. Ishikawa, M.; Hasegawa, Y.; Hatano, T.; Kunai, A.; Yamanaka, T. *Organometallics* **1989**, *8*, 2741.

(21) Stafstrom, S.; Bredas, J. L. *Phys. Rev. B.* **1988**, *38*, 4280.

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]

$$MO_2 + \tfrac{1}{2}B_4C + \tfrac{3}{2}C \rightarrow MB_2 + 2CO \tag{1}$$

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(1) For general reviews of the syntheses, structures, and properties of metal borides see: (a) Greenwood, N. N.; Parish, R. V.; Thornton, P. *Q. Rev.* **1966**, *20*, 441–464. (b) Matkovich, V. I. *Boron and Refractory Borides*; Springer-Verlag: New York, 1977. (c) Post, B. In *Boron, Metallo-Boron Compounds and Boranes*; Adams, R. M., Ed.; Interscience: New York, 1964; pp 301–372. (d) Greenwood, N. N. *The Chemistry of Boron*; Pergamon: New York, 1975; pp 697–731. (e) Thompson, R. In *Progress in Boron Chemistry*; Pergamon: New York, 1970; Vol. 2, pp 173–230. (f) Hoard, J. L.; Hughes, R. E. In *The Chemistry of Boron and Its Compounds*; Muetterties, E. L., Ed.; Wiley: New York, 1967; pp 25–154.

This method has been successfully applied to the large-scale preparation of, for example, hexaborides and tetraborides and to the diborides of most transition metals. This reaction, although efficient, is not useful for the syntheses of coatings or shaped materials since neither the metal oxides nor B_4C are soluble or meltable at reasonable temperatures.

The fact that several soluble processable polymeric precursors to boron carbide containing ceramics have now been developed[2] suggested to us that a processable precursor to a metal boride might be obtained by dispersing a metal source such as a metal oxide in a boron carbide polymeric precursor. Heating the mixture could then result in either the in situ generation of boron carbide and carbon followed by reaction to produce the boride or direct reaction of the polymer with the metal oxide to give the final boride product:

$$MO_2 + \text{polymer} \rightarrow B_4C + C + MO_2 \rightarrow MB_2 + CO \quad (2)$$

The key requirements of the polymer component are that it is stable and processable and contain both the boron needed to form the metal boride and carbon to aid in the removal of the oxygen. One series of polymers satisfying these criteria are the dinitrile polymers[3] $(\text{—}B_{10}H_{12}N{\equiv}C(CH_2)_aC{\equiv}N\text{—})_n$ (a = 5–8), which can be prepared in good yield from the condensation polymerization of decaborane(14) with dinitriles.

Two metal borides of particular interest for both structural and electronic applications are TiB_2 and ZrB_2, and there have recently been several reports of new chemical CVD precursors for the formation of films of these materials.[4] Since both borides have been produced by the reactions of their respective metal oxides with boron carbide,[5] as in eq 1, this suggested that the polymer approach described above in eq 2 might be successful. Indeed, we have now found that either TiO_2 or ZrO_2 powders may be dispersed in the decaborane–dinitrile polymer and that when these mixtures are heated to >1450 °C the corresponding diborides are formed in high chemical yields (>90% based on metal):

$$(\text{—}B_{10}H_{12}N{\equiv}C(CH_2)_5C{\equiv}N\text{—})_x + MO_2 \rightarrow MB_2 \qquad M = Ti, Zr \quad (3)$$

In a typical reaction, a precursor material, with a 1.0:2.4:1.7 mole ratio of Ti:B:C, was formed by dispersing 5.0 g of TiO_2 (1–2 μm, 99.999%) in a 50 mL of THF solution containing 3.89 g of the 1,5-dicyanopentane polymer $(\text{—}B_{10}H_{12}N{\equiv}C(CH_2)_5C{\equiv}N\text{—})_x$. The solution was then stirred vigorously while the solvent was vacuum evaporated to yield a yellow solid. A 0.87-g sample of this solid was then heated in a graphite boat in a tube furnace under an argon atmosphere at 1450 °C for 21 h. The resulting dark gray crystalline TiB_2 product (0.41 g) was obtained in 47.1% ceramic yield (theoretical ceramic yield, 48.9%), corresponding to a 96.3% chemical yield based on starting TiO_2. Pyrolysis of a 0.90-g sample of an analogous ZrO_2/polymer mixture (2.0 g of ZrO_2/1.5 g of polymer; 1.0:2.4:1.8, Zr:B:C ratio) at 1650 °C gave 0.53 g of crystalline ZrB_2 (ceramic yield 58.9%, theoretical 61.1%; chemical yield 96.4% based on ZrO_2).

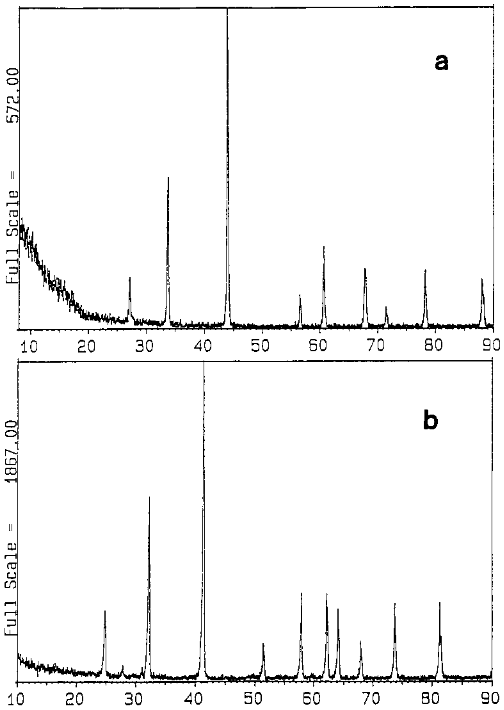

Figure 1. XRD spectra of (a) TiB_2 and (b) ZrB_2 powders prepared at 1450 and 1650 °C.

Elemental analyses of the products show excellent purities, with only very low levels of carbon, hydrogen, oxygen, and nitrogen.[6] The oxygen contents were found to further decrease at higher temperatures. The XRD spectra of the powders (Figure 1) indicate that they are highly crystalline and show no evidence for either unreacted MO_2 or for the formation of other ceramic materials, such as the metal nitrides, carbides, or other complex oxides (ie MBO_3).

As shown in the scanning electron micrographs in Figure 2, the powders formed at lower temperatures have a small grain size. Upon heating at 2000 °C, larger crystals were observed to form with an average size (estimated by SEM) of ~2–5 μm.

The TGA analysis (Figure 3) of the polymer/TiO_2 to TiB_2 conversion shows an initial ~8% weight decrease in the range 300–600 °C followed by a final loss at temperatures greater than 1200 °C. The initial loss is independent of the presence or identity of the metal oxide, consistent with a process, as indicated in eq 2, involving an initial polymer decomposition to a boron carbide/carbon material. This intermediate material then reacts at the higher temperatures with metal oxide to produce the metal boride products.

We have also found, depending upon the metal oxide particle size, polymer solution viscosity, and the presence of a suitable surfactant, that a MO_2/polymer precursor dispersion may be obtained that can then be used for the generation of metal boride coatings. We have, for example,

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[2] See, for example: (a) Mirabelli, M. G. L.; Sneddon, L. G. *J. Am. Chem. Soc.* **1988**, *110*, 3305. (b) Seyferth, D.; Rees, Jr., W. S.; Haggerty, J. S.; Lightfoot, A. *Chem. Mater.* **1989**, *1*, 45.

[3] Green, J.; Fein, M. M.; Mayes, N.; Donovan, G.; Israel, M.; Cohen, M. S. *Polym. Lett.* **1964**, *2*, 987–989.

[4] For examples see: (a) Jensen, J. A.; Gozum, J. E.; Pollina, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 1643. (b) Wayda, A. L., Schneemeyer, L. F.; Opila, R. L. *Appl. Phys. Lett.* **1988**, *53*, 361–363.

[5] (a) Kim, J. J.; McMurty, C. H. *Ceram. Eng. Sci. Proc.* **1985**, *6*, 1313–20. (b) Walker, J. K. *Adv. Ceram. Mater.* **1988**, *3*, 601–604.

[6] Anal. Calcd for TiB_2: Ti, 68.9%; B, 31.1%. Found for a 1450 °C sample: Ti, 68.9%; B, 29.9%; O, 1.4%; N, <0.2%; H, <0.2%; C, 0.14%. Found for a 2000 °C sample: Ti, 68.3%; B, 30.4%; O, 0.3%; N, 0.35%; H, <0.2%; C, 0.16%. Anal. Calcd for ZrB_2: Zr, 80.84%; B, 19.16%. Found for a 1650 °C sample: Zr, 80.3%; B, 18.5%; O, 1.53%; N, <0.1%; H, 0.2%; C, <0.03%. Found for a 2000 °C sample Zr, 80.3%; B, 19.2%; O, 0.2%; N, <0.1%; H, <0.1%; C, <0.14%. All elemental analyses were performed at Pascher, Remagen, West Germany.

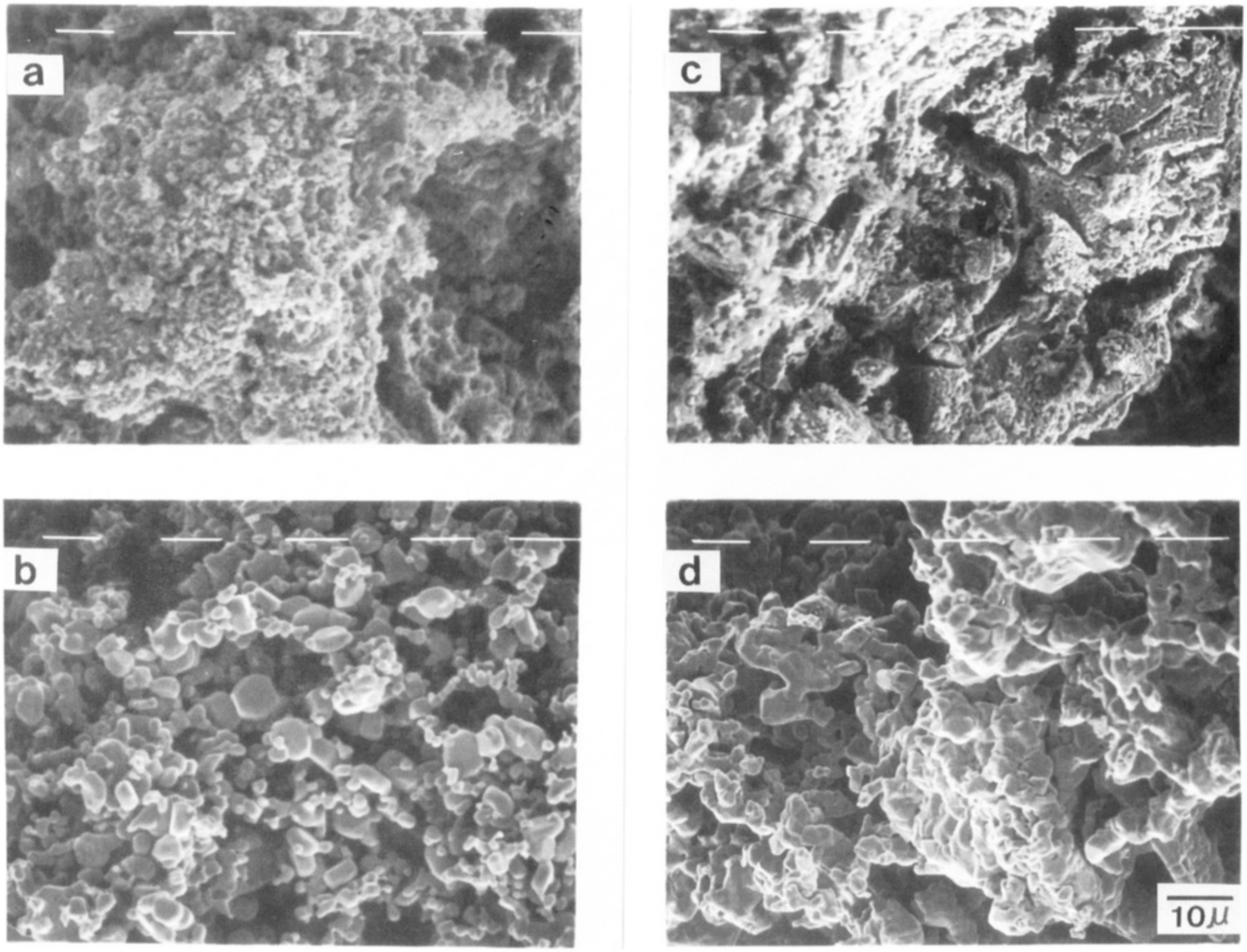

Figure 2. Scanning electron micrographs of TiB_2 ((a) 1450, (b) 2000 °C) and ZrB_2 ((c) 1650, (d) 2000 °C) powders.

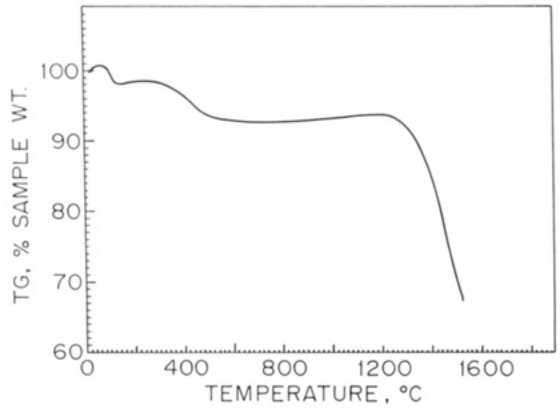

Figure 3. TGA analysis of the TiO_2/polymer to TiB_2 conversion. (Gas flow 100 cm^3/min Ar; heating rate, 10 °C/min.)

achieved TiB_2 coatings on graphite (POCO DFP-1) with this method.[7] Such coatings are of potential importance for many technological applications including, for example, the protection of carbon from attack by molten metals in composite materials. We are now in the process of expanding our studies of the application of this polymer precursor technique to the production of a wider variety of both metal borides and other non-oxide metal ceramics (e.g., silicides and nitrides) and to the generation of these materials in forms suitable for shaped and coated materials applications.

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Registry No. TiB_2, 12045-63-5; ZrB_2, 12045-64-6; TiO_2, 13463-67-7; ZrO_2, 1314-23-4; $(B_{10}H_{12}N{\equiv}C(CH_2)_5C{\equiv}N)_x$ (copolymer), 130574-33-3.

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[7] In a typical experiment, a coating precursor material was prepared by thoroughly mixing 0.15 g of submicron TiO_2 (Du Pont Marshall Laboratory) with 0.12 g of the decaborane polymer, ~0.05 g of Du Pont AB Dispersant, and 1.5 mL of THF. Solvent was removed until the desired viscosity was obtained and coatings could then be achieved by either dipping or by spreading the precursor mixture on the carbon substrate. Subsequent heating (2 °C/min) to 1450 °C produced a TiB_2 coating, as determined by Auger, XRD, and scanning electron microscopy.