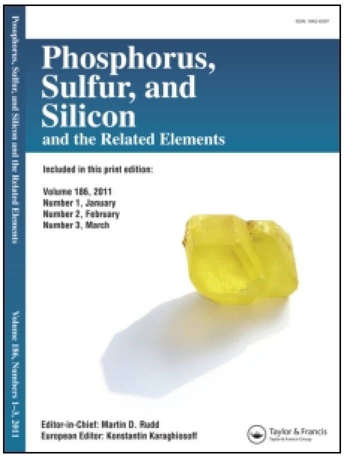

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

METAL-CATALYZED ROUTES TO RINGS, CHAINS, AND MACROMOLECULES BASED ON INORGANIC ELEMENTS

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To cite this Article Jaska, Cory A. , Bartole-Scott, Alexandra and Manners, Ian(2004) 'METAL-CATALYZED ROUTES TO RINGS, CHAINS, AND MACROMOLECULES BASED ON INORGANIC ELEMENTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 4, 685 — 694

To link to this Article: DOI: 10.1080/10426500490426403

URL: http://dx.doi.org/10.1080/10426500490426403

Phosphorus, Sulfur, and Silicon, 179:685–694, 2004
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490426403

METAL-CATALYZED ROUTES TO RINGS, CHAINS, AND MACROMOLECULES BASED ON INORGANIC ELEMENTS

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(Received August 18, 2003; accepted October 3, 2003)

Transition metal catalysis currently plays a profound role in organic synthesis, allowing for the controlled formation of C—C, C—N and C—O bonds in addition to many other useful transformations. In contrast, the development of analogous methods for the formation of homonuclear or heteronuclear bonds between inorganic elements is relatively unexplored. Nevertheless, the discovery of new synthetic methods, which can complement the classical reactions used in inorganic chemistry such as salt eliminations, is likely to be of key future importance for the general development of molecular and macromolecular inorganic chemistry.

The catalytic dehydropolymerization of silanes, germanes and stannanes originated through key discoveries in the mid 1980s, and is now well developed and represents a key advance.[1–5] More recently, homodehydrocoupling chemistry has been extended to include P—P bond formation,[6] and catalytic heterodehydrocoupling reactions to form, for example, B—Si,[7] Si—P,[8] and Si—O bonds[9,10] also have been reported. The use of metal complexes to catalyze ring-opening polymerization (ROP) reactions also represents a highly promising methodology to prepare macrocycles and polymers containing inorganic elements. For example, the discovery of late transition metal catalysts for the ROP of silaheterocycles was first discovered in the 1960s, with the advantage that

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I. M. thanks Cory Jaska and Alex Bartole for helping with a preliminary draft of this manuscript. I. M. also thanks the Petroleum Research Fund administered by the American Chemical Society and NSERC Discovery Grants program for funding this research.

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polymers such as polycarbosilanes can be formed under relatively mild conditions.[11,12]

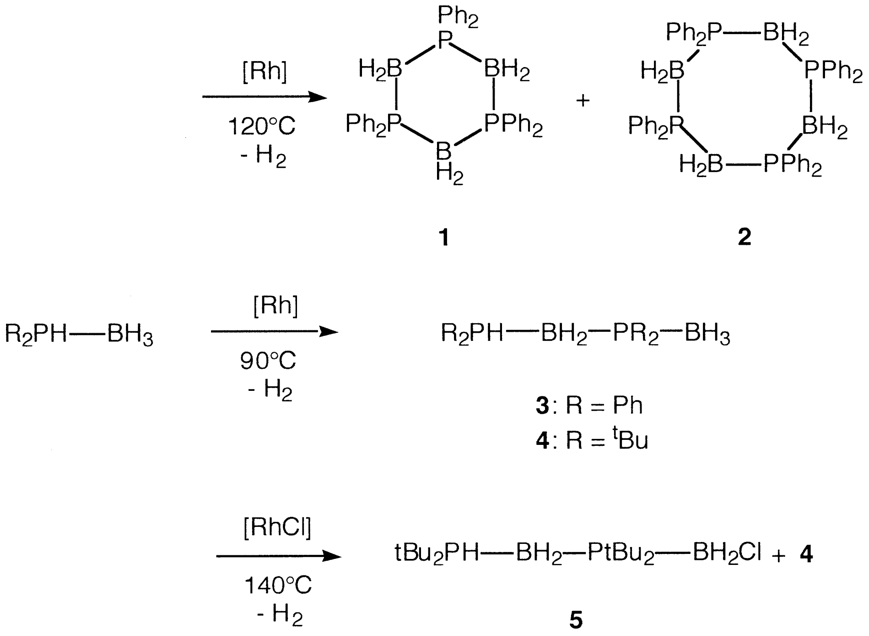
Our group has a fundamental interest in the development of new routes to rings, chains, and macromolecules based on main group and transition elements. Polymers containing inorganic elements are of particular importance as a result of their promise as functional macromolecular[13] and supramolecular[14] materials. In this article, some of our recent work on new catalytic routes is discussed.

CATALYTIC DEHYDROCOUPLING OF GROUP 13, GROUP 15 LEWIS ACID, LEWIS BASE ADDUCTS

The preparation of polymers with backbones of alternating phosphorus and boron atoms attracted significant attention in the 1950s and early 1960s as a consequence of their anticipated high thermal stability and resistance to oxidation and hydrolysis. The main synthetic route explored at that time involved thermally-induced dehydrocoupling of phosphine-borane adducts at 180–200°C, to afford predominantly six-membered rings. Only negligable yields of low molecular weight, partially characterized polymers were claimed, mainly in patents.[15] We recently have shown that the dehydrocoupling process can be catalyzed by late transition metal complexes. This has permitted the formation of six- and eight-membered phosphinoborane rings under more facile conditions, novel linear oligomeric chains, and high molecular weight polyphosphinoboranes.

Catalytic Dehydrocoupling of Secondary Phosphine-Borane Adducts

The uncatalyzed dehydrocoupling of the secondary phosphine-borane adduct $Ph_2PH{\cdot}BH_3$ at 170°C gives a mixture of the cyclic trimer $[Ph_2\,P{-}BH_2]_3$ (**1**) and tetramer $[Ph_2P{-}BH_2]_4$ (**2**) in an 8:1 ratio. However, upon heating $Ph_2PH{\cdot}BH_3$ in the presence of $[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$ or $[Rh(1,5\text{-}cod)_2][OTf]$ (0.5–1 mmol% Rh) at 120°C, **1** and **2** are formed in a 2:1 ratio (Scheme 1). Upon lowering the temperature to 90°C, the novel linear compound $Ph_2PH\text{-}BH_2{-}PPh_2{-}BH_3$ (**3**) was formed as the exclusive product (Scheme 1).[16,17] In the absence of catalyst at 90°C, no conversion of $Ph_2PH{\cdot}BH_3$ was observed; at 120°C, no cyclic products and only a minor amount (<5%) of 3 was observed. The activity of other transition metal complexes also was demonstrated but Rh(I) and Rh(III) complexes were found to be the best precatalysts.[17]



1 **2**

3: R = Ph
4: R = ^{t}Bu

5

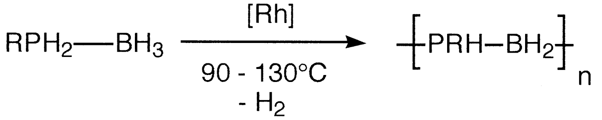
[Rh] = Rhodium Catalyst
[RhCl] = Chlorine containing Rh Catalyst

SCHEME 1

Heating of the sterically encumbered adduct $^t\mathrm{Bu_2PH{\cdot}BH_3}$ in the presence of [Rh(1,5-cod)$_2$][OTf] or $\mathrm{Rh_6(CO)_{16}}$ at 140°C also results in dehydrocoupling to form the linear compound $^t\mathrm{Bu_2PH{-}BH_2{-}P^tBu_2{-}BH_3}$ (**4**). The use of the chlorinated catalysts [Rh(μ-Cl)(1,5-cod)]$_2$ or $\mathrm{RhCl_3{\cdot}3H_2O}$ at 160°C was found to give an inseparable mixture of **4** and the chlorinated compound $^t\mathrm{Bu_2PH{-}BH2{-}P^tBu_2{-}BH_2Cl}$ (**5**) (Scheme 1).[18]

Catalytic Dehydrocoupling of Primary Phosphine-Borane Adducts; Synthesis of Polyphosphinoboranes

In the early 1960s the uncatalyzed pyrolysis of the primary phosphine-borane adduct $\mathrm{PhPH_2{\cdot}BH_3}$ at 100–150°C for 13 h was reported to give a benzene-soluble polymer $[\mathrm{PhPH{-}BH_2}]_n$ with a molecular weight (M_n) of 2,150. Prolonged heating at elevated temperatures (250°C) led to the formation of insoluble material, without significant molecular weight



$$RPH_2—BH_3 \xrightarrow[90\text{ - }130°C \\ \text{- }H_2]{[Rh]} \left[PRH—BH_2 \right]_n$$

6: R = Ph
7: R = ^iPr
8: R = p-$^nBuC_6H_4$
9: R = p-dodecylC_6H_4

SCHEME 2

increase of the benzene-soluble fraction (maximum $M_n = 2{,}630$).[19] We found that heating of a toluene solution of $PhPH_2 \cdot BH_3$ at reflux (110°C) in the presence of [Rh(1,5-cod)$_2$][OTf] (0.5–1 mmol% Rh) for 15 h led to dehydrogenative coupling to afford poly(phenylphosphinoborane) $[PhPH—BH_2]_n$ (**6**) as an off-white powder (Scheme 2).[16,17] Static light scattering (SLS) of **6** in THF showed the material to be of relatively low molecular weight of $M_w = 5{,}600$. However, dehydrocoupling in the absence of solvent and modification of the reaction temperatures led to higher molecular weight polymer. Thus, neat $PhPH_2{\cdot}BH_3$ in the presence of [Rh(—Cl)(1,5-cod)]$_2$ or $RhCl_3 \cdot 3H_2O$ (0.6 mmol% Rh) was heated at 90°C for 3 h, and then at 130°C for 3 h. The reaction mixture gradually became viscous during the heating stage at 90°C and completely solidified after 3 h at 130°C. The polymer obtained was spectroscopically identical to the material prepared in toluene, but SLS confirmed a higher molecular weight of $M_w = 33{,}300$.

Prolonged heating of **6** at 130°C in the presence of catalyst afforded insoluble products that were found to swell significantly in THF or CH_2Cl_2. As branching positions could not be detected in the ^{31}P and ^{11}B NMR spectra, the polymers may either become weakly crosslinked through additional interchain P—B coupling, or may increase in molecular weight above the solubility limit. We confirmed that in the absence of a transition metal-catalyst, the thermally-induced dehydrocoupling of $PhPH_2{\cdot}BH_3$ proceeds very slowly and forms only low molecular weight materials.[17]

Several other primary phosphine-borane adducts have been shown to undergo metal-catalyzed dehydrocoupling to form polyphosphinoboranes (**7**: R = ^iBu; **8**: p-$^nBuC_6H_4$; **9**: p-dodecyl-C_6H_4; Scheme 2). The alkyl substituted adduct $^iBuPH_2{\cdot}BH_3$ was found to require more forcing dehydrocoupling conditions (15 h at 120°C) in order to form **7**.[17,20] This is likely due to the decreased polarity of the P—H bond as a result of the strong (+)-inductive effect of the alkyl group. SLS studies of **7** in THF gave molecular weight values of $M_w = 13{,}100$. In contrast to **6** and **7**, molecular weight analysis of **8** and **9** by GPC gave M_w values of ca. 19,000 and 168,000 (relative to polystyrene standards) respectively.

Wide-angle x-ray scattering of solution cast films of **6** and **8** indicated that the polymers were essentially amorphous.[20] This was expected, as the dehydropolymerization process should not provide any stereochemical control, and thus atactic polymers would result. Thermogravimetric analysis of **6** indicated the onset of decomposition at 160°C with a ceramic yield of 75–80% upon heating to 1000°C.[20] Lower onset temperatures of 120°C were found for both **7** and **8**. Substantial weight loss was observed upon heating to 1000°C, resulting in moderate ceramic yields of 40–45% and 35–40% for **7** and **8** respectively. The high ceramic yield of **6** suggests that it may function as a useful preceramic polymer for BP based materials.[20] Indeed, preliminary pyrolysis studies of **6** at 1000°C under nitrogen show the formation of boron phosphide as the major crystalline component by powder x-ray diffraction.

Current work aims to provide an understanding of the dehydropolymerization mechanism.[21–23] and the generalization of this catalytic dehydrocoupling methodology to other group 13/15 systems.[24,25]

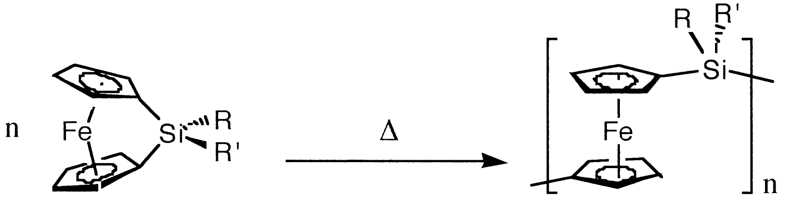
CATALYTIC ROP OF CYCLIC THIONYLPHOSPHAZENES

Our group also has been interested in the possibility of creating new macromolecular chains based on main group elements using ROP processes. We have found, for example, that the cyclic thionylphosphazene $[NSO(NPCl_2)_2]$ thermally polymerizes at 165°C to yield poly(pentachlorothionylphosphazene) $[NSO(NPCl_2)_2]_n$, which undergoes halide substitution in a manner similar to poly(dichlorophosphazene) (e.g., with amines) to form hydrolytically stable sulfur-nitrogen-phosphorus polymers.[26,27] Mechanistic studies of the process suggested a cationic, chain growth ROP mechanism. We have found that the ROP can be performed at room temperature by using halide-accepting, Lewis acids as catalysts (e.g., $GaCl_3$).[28] Interestingly, the polymerization shows a dramatic dependence on monomer concentration, with no polymer formed below a concentration of 0.15 M. This is characteristic of a weakly exothermic polymerization which indicates that the monomer **20** is virtually unstrained.[28] The mechanism for the catalytic ROP is currently under study. Abstraction of the Cl substituent at the sulphur(VI) center to generate a thionylphosphazene cation may well be involved.[28]

Polythionylphosphazenes represent an interesting class of main group polymers with tunable properties. The backbone is stable to hydrolysis and even water soluble derivatives have been made. The high gas permeability of some of these materials has led to interest in their use as matrices for luminescent, oxygen sensors.[29]

CATALYTIC ROP OF [1]FERROCENOPHANES AND SI-BRIDGED BIS(BENZENE)CHROMIUM COMPLEXES

We initiated studies on ring-opening polymerization (ROP) routes to metal-containing polymers approximately a decade ago. We targeted potential monomers with strained structures so that ROP would be thermodynamically favourable. Among the species studied were silicon-bridged [1]ferrocenophanes **22** ([1]silaferrocenophanes), the first examples of which were prepared by Osborne and coworkers in England in the mid 1970s.[30] These strained molecules are readily available on a substantial (>100 g) scale from the reaction of dilithioferrocene.tetramethylethylenediamine ($fcLi_2$. TMEDA) with dichloroorganosilanes $RR'SiCl_2$. We found that these species polymerized when heated in the melt in sealed evacuated tubes at 120–150°C to afford high molecular weight ($M_n > 10^5$) polyferrocenylsilanes **23** (Scheme 3).[31]



R,R' = alkyl, aryl, H, Cl, etc. R,R' = alkyl, aryl, H, Cl, etc.

SCHEME 3

Since the initial ROP discovery, we and others have expanded this ROP methodology to a range of analogous strained monomers which contain other single-atom bridges (E = Ge, P, Sn, S etc.), two-atom bridges (E = C—C, C—P, C—S etc.) and transition metals (e.g. Ru, Cr) and/or different π-hydrocarbon rings (arenes).[32,33] The potential applications of many of these polymers as, for example, redox-active materials with uses in colloidal crystal photonic devices, thermal precursors to magnetic films, micro- and nanostructures, liquid crystalline materials, charge dissipative coatings, variable refractive-index sensing materials, are currently under study.[34,35]

Thermal ROP provides an excellent method for preparing high molecular weight polymetallocenes but the polydispersities are broad (PDIs = 1.5–2.5) and no control of molecular weight has been possible to date.[31,32] Subsequently, living anionic ROP routes to polymetallocenes using initiators such as nBuLi at ambient or subambient temperatures have been developed.[36,37] These methods have permitted unprecedented control of main chain metal-containing polymer architectures. In particular, materials with controlled molecular weights and narrow molecular weight distributions and access provided to the first block copolymers with metals in the main chain have been prepared. This has created unique opportunities for the generation of self-assembled, supramolecular materials. However, stringent experimental requirements need to be met for anionic ROP to be successful. Due to the low concentration of highly reactive anionic chain propagating sites, impurity levels need to be extremely low. This led to interest in similarly mild but more convenient methods for preparing polymetallocenes via ROP.

Transition metal-catalyzed ROP of silicon-bridged [1]ferrocenophanes was reported in 1995 and occurs in solution at room temperature in the presence of Pt^{II}, Pt^0, Rh^I, and Pd^{II} precatalysts.[38,39] Transition metal catalyzed ROP is a mild method which, significantly, has the key advantage over anionic methods in that extensive monomer and solvent purification is unnecessary. This route has now been developed to the stage where considerable control over polymetallocene architectures is possible.[40,41] For example, [1]silaferrocenophanes with different cyclopentadienyl rings can undergo regioregular transition metal catalyzed ROP whereas thermal ROP affords a regioirregular PFS material.[416]

Transition metal-catalyzed ROP of silicon-bridged [1]ferrocenophanes in the presence of Si—H containing species such as Et_3SiH allows the formation of PFSs **24** with a molecular weight control dictated by the initial ratio of monomer to silane (Figure 3). However, unlike the case of anionically ring-opened materials, the polydispersities are appreciable (typically ca. 1.4–1.5 versus <1.1).[40,41] This transition metal-catalyzed ROP methodology has been extended toward the formation of comb and star copolymers with the appropriate Si—H source.[41]

Most recently we have found that transition metal catalysis allows the ROP of strained organometallic species such as silicon-bridged bis(benzene)chromium complexes. These monomers are very difficult to polymerize by other means such as thermal or anionic polymerization. However, in the presence of Pt(0) catalysts, ROP proceeds smoothly to yield the first homopolymers of with bis(benzene)chomium and organosilane spacers in the main chain.[42]

The mechanism of the platinum-catalyzed ROP of [1]silaferrocenophanes is of intense interest in our research group and is believed to involve colloidal platinum at the true catalyst.[43]

SUMMARY

Metal-catalyzed processes appear to show exceptional potential for the creation of new macromolecules based on inorganic elements. Further studies of the mechanism of these reactions are critical to allow more efficient and general catalysts to be developed. Of particular significance is the potential to generate polymers with controlled molecular weights and with interesting architectures such as block copolymers. These materials offer exceptional opportunities for the creation of novel supramolecular materials via self-assembly processes.[14]

REFERENCES

[1] F. Gauvin, J. F. Harrod, and H.-G. Woo, *Adv. Organomet. Chem.*, **42,** 363 (1998).

[2] C. Aitken, J. F. Harrod, and E. Samuel, *J. Am. Chem. Soc.*, **108,** 4059 (1986).

[3] J. A. Reichl and D. H. Berry, *Adv. Organomet. Chem.*, **43,** 197 (1999).

[4] T. Imori, V. Lu, H. Cai, and T. D. Tilley, *J. Am. Chem. Soc.*, **117,** 9931 (1995).

[5] J. A. Reichl, C. M. Popoff, L. A. Gallagher, E. E. Remsen, and D. H. Berry, *J. Am. Chem. Soc.*, **118,** 9450 (1996).

[6] a) N. Etkin, M. C. Fermin, and D. W. Stephan, *J. Am. Chem. Soc.*, **119,** 2954 (1997); b) V. P. W. Böhm and M. Brookhart, *Angew. Chem. Int. Ed.*, **40,** 4694 (2001).

[7] Q. A. Jiang, P. J. Carroll, and D. H. Berry, *Organometallics*, **12,** 177 (1993).

[8] R. Shu, L. Hao, J. F. Harrod, H.-G. Woo, and E. Samuel, *J. Am. Chem. Soc.*, **120,** 12988 (1998).

[9] Y. Li and Y. Kawakami, *Macromolecules*, **32,** 6871 (1999).

[10] R. Zhang, J. E. Mark, and A. R. Pinhas, *Macromolecules*, **33,** 3508 (2000).

[11] a) D. R. Weyenberg and L. E. Nelson, *J. Org. Chem.*, **30,** 2618 (1965); b) N. S. Nametkin, V. M. Vdovin, K. S. Pushchevaya, and V. I. Zavylov, *Bull. Acad. Sci. USSR*, 1411 (1965); c) W. A. Kriner, *J. Polym. Sci., Part A-1*, **4,** 444 (1966); d) W. R. Bamford, J. C. Lovie, and J. A. C. Watt, *J. Chem. Soc. (C)*, 1137 (1966); e) C. S. Cundy and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 445 (1972).

[12] a) H. Yamashita, M. Tanaka, and K. Honda, *J. Am. Chem. Soc.*, **117,** 8873 (1995); b) X. Wu and D. C. Neckers, *Macromolecules*, **32,** 6003 (1999); c) M. Lienhard, I. Rushkin, G. Verdecia, et al., *J. Am. Chem. Soc.*, **119,** 12020 (1997).

[13] R. D. Archer, *Inorganic and Organometallic Polymers* (Wiley-VCH, Weinheim, 2001); b) I. Manners, *Angew. Chem. Int. Ed.*, **35,** 1602 (1996); c) P. Nguyen, P. Gómez-Elipe, and I. Manners, *Chem. Rev.*, **99,** 1515 (1999).

[14] a) I. Manners, *Science*, **294,** 1664 (2001); b) J.-F. Gohy, B. G. G. Lohmeijer, S. K. Varshney, and U. S. Schubert, *Macromolecules*, **35,** 7427 (2002); c) S. Hou and W. K. Chan, *Macromol. Rapid Commun.*, **20,** 440 (1999); d) K. Temple, K. Kulbaba, K. N. Power-Billard, et al., *Adv. Mater.*, **15,** 297 (2003); e) J. A. Massey, M. A. Winnik,

I. Manners, et al., *J. Am. Chem. Soc.*, **123,** 3147 (2001); f) C. M. Park, J. E. McAlvin, C. L. Fraser, and E. L. Thomas, *Chem. Mater.*, **14,** 1225 (2002).

[15] a) A. B. Burg, *J. Inorg. Nucl. Chem.*, **11,** 258 (1959); b) A. B. Burg and R. I. Wagner, 1963, U. S. Pat. 3,071,553.

[16] H. Dorn, R. A. Singh, J. A. Massey, A. J. Lough, and I. Manners, *Angew. Chem. Int. Ed.*, **38,** 3321 (1999).

[17] H. Dorn, R. A. Singh, J. A. Massey, et al., *J. Am. Chem. Soc.*, **122,** 6669 (2000).

[18] H. Dorn, E. Vejzovic, A. J. Lough, and I. Manners, *Inorg. Chem.*, **40,** 4327 (2001).

[19] V. V. Korshak, V. A. Zamyatina, and A. I. Solomatina, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, **8,** 1541 (1964).

[20] H. Dorn, J. M. Rodezno, B. Brunnhöfer, et al., *Macromolecules*, **36,** 291 (2003).

[21] J.-M. Denis, H. Forintos, H. Szelke, et al., *Chem. Commun.*, 54 (2003).

[22] H. Dorn, C. A. Jaska, R. A. Singh, A. J. Lough, and I. Manners, *Chem. Commun.*, 1041 (2000).

[23] C. A. Jaska, H. Dorn, A. J. Lough, and I. Manners, *Chem. Eur. J.*, **9,** 271 (2003).

[24] C. A. Jaska, K. Temple, A. J. Lough, and I. Manners, *Chem. Commun.*, 962 (2001).

[25] C. A. Jaska, K. Temple, A. J. Lough, and I. Manners, *J. Am. Chem. Soc.*, **125,** 9424 (2003).

[26] M. Liang and I. Manners, *J. Am. Chem. Soc.*, **113,** 4044 (1991).

[27] Y. Z. Ni, P. Park, M. Liang, J. A. Massey, C. Waddling, and I. Manners, *Macromolecules*, **29,** 3401 (1996).

[28] a) D. P. Gates, M. Edwards, L. M. Liable-Sands, A. L. Rheingold, and I. Manners, *J. Am. Chem. Soc.*, **120,** 3249 (1998); b) A. R. McWilliams, D. P. Gates, M. Edwards, et al., *J. Am. Chem. Soc.*, **122,** 8848 (2000).

[29] a) Z. Pang, X. Gu, A. Yekta, et al., *Adv. Mater.*, **8,** 768 (1996); b) Z. Wang, A. R. McWilliams, C. E. B. Evans, et al., *Adv. Func. Mater.*, **12,** 415 (2002).

[30] A. G. Osborne and R. H. Whiteley, *J. Organomet. Chem.*, **101,** C27 (1975).

[31] D. A. Foucher, B. Z. Tang, and I. Manners, *J. Am. Chem. Soc.*, **114,** 6246 (1992).

[32] a) R. Rulkens, D. P. Gates, J. K. Pudelski, et al., *J. Am. Chem. Soc.*, **119,** 10976 (1997); b) R. Resendes, J. M. Nelson, A. Fischer, et al., J. *Am. Chem. Soc.*, **123,** 2116 (2001); c) T. Baumgartner, F. Jäkle, R. Rulkens, et al., *J. Am. Chem. Soc.*, **124,** 10062 (2002).

[33] a) H. K. Sharma, F. Cervantes-Lee, J. S. Mahmoud, and K. H. Pannell, *Organometallics*, **18,** 399 (1999); b) T. Mizuta, Y. Imamura, and K. Miyoshi, *J. Am. Chem. Soc.*, **125,** 2068 (2003).

[34] D. A. Foucher, C. H. Honeyman, J. M. Nelson, B. Z. Tang, and I. Manners, *Angew. Chem. Int. Ed. Engl.*, **32,** 1709 (1993); b) J. K. Pudelski, R. Rulkens, D. A. Foucher, et al., *Macromolecules*, **28,** 7301 (1995); c) X. H. Liu, D. W. Bruce, and I. Manners, *Chem. Commun.*, 289 (1997); d) M. Ginzburg, J. Galloro, F. Jäkle, et al., *Langmuir*, **16,** 9609 (2000); e) R. Rulkens, R. Perry, A. J. Lough, et al., *J. Am. Chem. Soc.*, **118,** 12683 (1996); f) R. Resendes, A. Berenbaum, G. Stojevic, et al., *Adv. Mater.*, **12,** 327 (2000); g) M. J. MacLachlan, M. Ginzburg, N. Coombs, et al., *Science* **287,** 1460 (2000); h) A. Arsenault, H. Miguéz, V. Kitaev, G. A. Ozin, and I. Manners, *Adv. Mater.*, **15,** 503 (2003); i) A. Berenbaum, M. Ginzburg-Margau, N. Coombs, et al., *Adv. Mater.*, **15,** 51 (2003).

[35] a) S. Barlow, A. L. Rohl, S. Shi, C. M. Freeman, and D. O'Hare, *J. Am. Chem. Soc.*, **118,** 7578 (1996); b) V. S. Papkov, M. V. Gerasimov, I. I. Dubovik, et al., *Macromolecules*, **33,** 7107 (2000); c) Q. Sun, J. W. Y. Lam, K. Xu, et al., *Chem. Mater.*, **12,** 2617 (2000); d) L. I. Espada, M. Shadaram, J. Robillard, and K. H. Pannell, *J. Inorg. Organomet. Polym.*, **10,** 169 (2000); e) G. Calléja, G. Cerveau, and R. J. P. Corriu, *J. Organomet. Chem.*, **621,** 46 (2001).

[36] a) R. Rulkens, A. J. Lough, and I. Manners, *J. Am. Chem. Soc.*, **116,** 797 (1994); b) Y. Ni, R. Rulkens, and I. Manners, *J. Am. Chem. Soc.*, **118,** 4102 (1996).

[37] T. J. Peckham, J. A. Massey, C. H. Honeyman, and I. Manners, *Macromolecules*, **32,** 2830 (1999).

[38] Y. Ni, R. Rulkens, J. K. Pudelski, and I. Manners, *Macromol. Rapid Commun.*, **16,** 637 (1995).

[39] N. P. Reddy, H. Yamashita, and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, 2263 (1995).

[40] P. Gómez-Elipe, P. M. Macdonald, and I. Manners, *Angew. Chem. Int. Ed. Engl.*, **36,** 762 (1997).

[41] P. Gómez-Elipe, R. Resendes, P. M. Macdonald, and I. Manners, *J. Am. Chem. Soc.*, **120,** 8348 (1998).

[42] a) A. Berenbaum and I. Manners, unpublished results (2002), b) K. C. Hultzsch, J. M. Nelson, A. J. Lough, and I. Manners, *Organometallics*, **14,** 5496 (1995).

[43] K. Temple, F. Jäkle, J. B. Sheridan, and I. Manners, *J. Am. Chem. Soc.*, **123,** 1355 (2001).