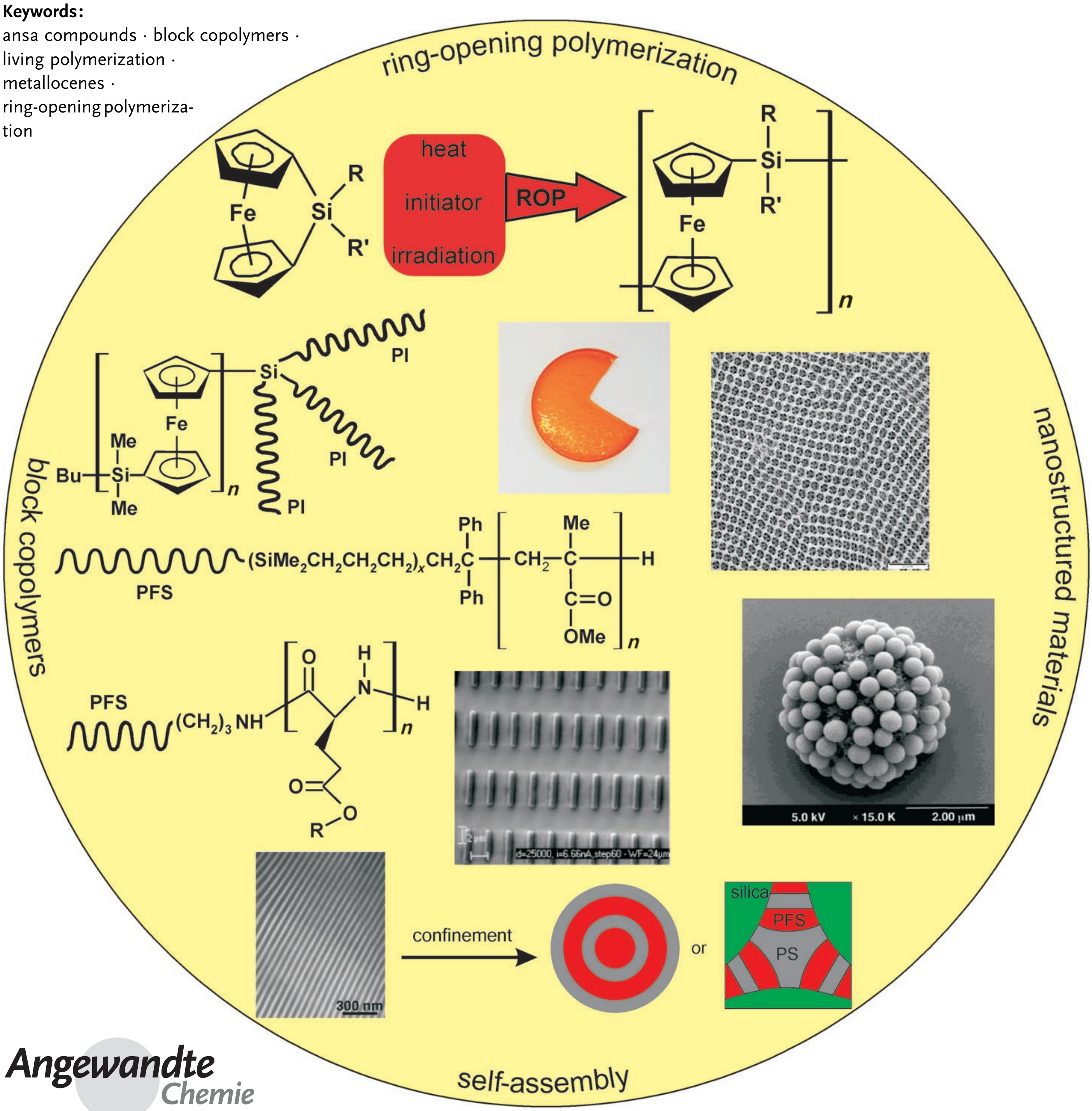
DOI: 10.1002/anie.200604420

Metallocenophane Polymerization

Polyferrocenylsilane-Based Polymer Systems

*Vasilios Bellas and Matthias Rehahn**

Keywords:
ansa compounds · block copolymers · living polymerization · metallocenes · ring-opening polymerization



Angewandte Chemie

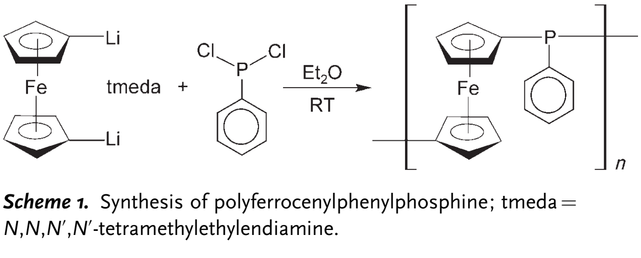
The study of metallopolymers has blossomed into a mature field over the last few decades. Especially, polyferrocenylsilane (PFS) chemistry has taken a tremendous leap and continues to raise intense interest. Since the discovery of thermal ring-opening polymerization (ROP) of sila[1]ferrocenophanes, PFSs have been also accessed by anionic, cationic, transition-metal-catalyzed, and photolytic anionic ROP methodologies. A plethora of synthetic strategies have been devised, enabling access to a wide variety of copolymers, polyelectrolytes, and nanostructured materials. The distinctive physical properties and functions of many PFS-based polymers have been explored, leading to their apt exploitation in technical applications. Therefore, it is conceivable that PFS-related platforms might be indispensable nano-objects in the near future, as they stand on the verge of a new generation of sophisticated materials.

From the Contents

1. Introduction—A Retrospective View

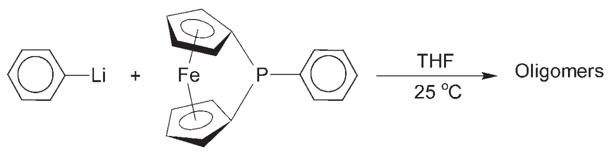
Several books and comprehensive reviews have been devoted to organometallic polymers.[1] In particular, there is a vigorous research activity about polyferrocenylsilane (PFS) materials in contemporary macromolecular science.[2] The scope of this article is to provide a summary of the topic, supplementing the existing reviews by highlighting the recently added achievements as well as the far-reaching potential of PFS-based scaffolds. Whereas the facile ring-opening polymerization (ROP) of various ferrocenophanes (FCPs) is described in a plethora of reports, scarce examples exist in the case of related ansa complexes, which are at a much more primitive stage of development. Therefore, the structural parameters that govern the ROP process of ansa complexes are also briefly discussed. Moreover, this article is complementary to the Review by Manners et al. in this issue, which is focused on strained metallocenophanes and related organometallic rings, with special emphasis on small-molecule aspects.[3]

The field of the metal-containing polymers was opened at DuPont in 1955 with the synthesis of polyvinylferrocene by radical polymerization.[4] During the next decades the progress in the synthesis of metallopolymers was tremendous, with the overwhelming majority to be low-molecular-weight polymers, mainly metallocene-based. In the early 1980s Seyferth and co-workers[5] described the synthesis of high-molecular-weight ferrocenylphenylphosphine polymers (M_w up to 161 kDa) by treating $\mathrm{PPhCl_2}$ with 1,1′-dilithioferrocene under appropriate conditions (Scheme 1).



Scheme 1. Synthesis of polyferrocenylphenylphosphine; tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylendiamine.

This result is quite unexpected for such a polycondensation reaction, owing to the inherent limitations of the step-growth process to access high number-average degrees of polymerization, that is, the requirements of highest purity of monomers, exact equivalence of functional groups, and actually quantitative conversion. Nevertheless, no explanation was proposed, and no speculation was expressed about the probable in situ formation of the corresponding phosphorous-bridged [1]FCP and its subsequent [fcLi$_2$·$^2\!/_3$tmeda]-initiated anionic ROP (fc = 1,1′-ferrocendiyl). In the same paper, it is reported that linear oligomers were isolated when the phosphorus-bridged [1]FCP was treated with phenyllithium in ethereal solvents, regardless of the concentration of the anionic initiator (Scheme 2).

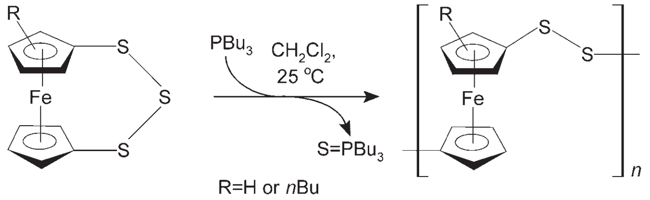


Scheme 2. Attempted anionic ROP of [1]ferrocenylphenylphosphine.

The unsuccessful anionic ROP was attributed either to steric effects or to insolubility. Maybe as a result of this explanation serious investigation into the synthesis of related structures was hindered for nearly ten years until Rauchfuss and Brandt published the synthesis of poly(ferrocenylene persulfides) from the unstrained trithia[3]ferrocenophane by a novel atom-abstraction based ROP pathway.[6] Desulfuriza-

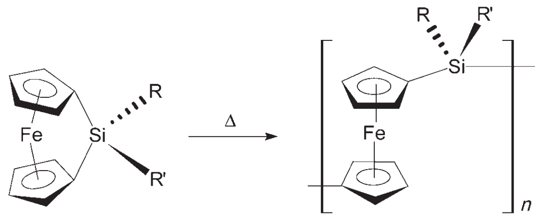
---

[*] Dr. V. Bellas, Prof. Dr. M. Rehahn
Ernst-Berl Institute for Chemical Engineering and Macromolecular Science
Darmstadt University of Technology
Petersenstrasse 22, 64287 Darmstadt (Germany)
Fax: (+49) 6151-16-4670
E-mail: mrehahn@dki.tu-darmstadt.de



Scheme 3. Synthesis of poly(ferrocenylene persulfides).

tion takes place in the presence of one equivalent of $n\mathrm{Bu}_3\mathrm{P}$ (Scheme 3).



Scheme 4. Thermal ROP of sila[1]ferrocenophanes.

A few months later new prospects on the field were opened up as a result of the synthesis of high-molecular-weight PFSs through the thermal ROP of the corresponding silicon-bridged [1]FCPs, marking a major milestone in the history of organometallic polymers (Scheme 4). The first report on this important achievement was published by Manners et al. in 1992; a few months later, similar results were described by Pannell et al.[7] The Manners group had initially focussed on the ROP behavior of the disilane-bridged [2]FCP, concluding that these species are reluctant to undergo thermal ROP.[8] Therefore, they decided to access relevant structures through the Wurtz coupling of $[\mathrm{fc(SiMe_2Cl)_2}]$. However, the reaction between $[\mathrm{fcLi_2}\cdot{}^2\!/_3\mathrm{tmeda}]$ and two equivalents of $\mathrm{Me_2SiCl_2}$ afforded an orange polymer rather than the anticipated disubstituted ferrocene derivative. Motivated by curiosity, they analyzed the polymer, whereupon a 1:1 ratio of ferrocene units to $\mathrm{SiMe_2}$ groups was revealed, contrary to the expected 1:2 ratio according to the reaction stoichiometry. Since the molecular weight was well over 300 kDa, they suspected that a chain-growth reaction took place involving the ROP of the in situ formed dimethylsila[1]ferrocenophane. This assumption was confirmed by repeating the reaction of $[\mathrm{fcLi_2}\cdot{}^2\!/_3\mathrm{tmeda}]$ and $\mathrm{Me_2SiCl_2}$ in an equamolar ratio, leading to isolation of the strained [1]FCP, and finally thermal treatment at 130°C, thereby providing an amber solid material, identified as PFS.

2. Ring-Opening Polymerization

2.1. The Paramount Importance of Ring-Opening Polymerization

Since many interesting polymer properties are accessible only if the molecular weight exceeds a certain value, powerful synthetic pathways are needed to reach the desirable chain length. Conventional polycondensation routes are unable to produce high-molecular-weight metallopolymers. This failure arises from the difficulty to achieve both high purity levels of the reactive organometallic species and precise stoichiometry between the monomers. Therefore, such polycondensation reactions usually do not proceed to near completion, causing the formation of low-molecular-weight macromolecular chains only.

It is noteworthy that the first efforts to prepare PFS by polycondensation routes were patented in the 1960s.[9] Two different pathways were used: the first one involved condensation of $\mathrm{FeCl_2}$ with $\mathrm{Li_2[(C_5H_4)_2SiMe_2]}$, while in the other 1,1′-dilithioferrocene was treated with $\mathrm{R_2SiCl_2}$ (R = Me or Ph). However, both methods afforded low-molecular-weight samples. Later on, the same strategy was exploited for the synthesis of polyferrocenylstannanes from dilithioferrocene and $\mathrm{R_2SnCl_2}$ (R = Me, Et, nBu, or Ph).[10]

On the other hand, chain-growth processes enable the synthesis of high-molecular-weight polymers even at low levels of monomer conversion, owing to the rather high reactivity of the propagating species. ROP reactions represent an efficient way for the formation of high-molecular-weight polymers, as they occur through a chain-growth mechanism. ROP is used successfully for the synthesis of a wide variety of inorganic polymers, such as polycarbosilanes, polysiloxanes, polysilanes, polysilazanes, and polyphosphazenes.[11] In contrast, although a plethora of metal-containing rings exist, there are limited studies concerning their polymerization behavior. The first reports for the ROP synthesis of polymers bearing transition metals in the backbone appeared in 1989 by Roesky and Lücke, and are the only reported before the

Vasilios Bellas, born in 1976 in Athens, Greece, received degrees in chemistry and polymer science from the Universities of Ioannina and Athens, respectively. He completed his PhD thesis at the NCSR "Demokritos" working on silsesquioxane-based resist materials suitable for high-resolution lithography. Since November 2004 he has been a postdoctoral researcher in Prof. M. Rehahn's group at Darmstadt University of Technology. His current research interests lie in the synthesis of well-defined PFS block copolymers with complex architectures.

Matthias Rehahn, born in 1961 in Frankfurt/Main, Germany, studied Chemistry at the University of Mainz. His PhD thesis was carried out at the Max-Planck Institute for Polymer Research, Mainz. After a postdoctoral stay at the ETH Zürich, he completed his habilitation at the University of Karlsruhe. Since 1999 he is full professor at the Darmstadt University of Technology and head of the German Institute for Polymers (DKI). Current fields of research include ionic and transition-metal-catalyzed polymerizations, functional polymers for optoelectronics, and polyelectrolytes.

discovery of polymerizable FCPs.[12] Roesky and Lücke synthesized $[\{(C_5Me_5)TaN(Cl)\}_n]$ and $[\{\text{-}N{=}MCl_3\text{-}N{=}P(Ph_2)\text{-}N{=}P(Ph_2)\text{-}\}_n]$ in refluxing xylene from the corresponding cyclic metal nitride and metallophosphazenes (M = Mo or W), respectively.

2.2. Ring-Opening Polymerization Behavior of Ansa Compounds

The deviation from an unstrained sandwich structure with an ideal coplanar ring orientation can be described with the angles α, β, θ, and δ (Figure 1). [1]Metallocenophanes with a large dihedral angle between the two cyclopentadienyl (Cp) rings (tilt angle, α) are highly strained and strongly susceptible to strain release by undergoing ROP reactions. In such ansa complexes the linkage between the two carbon rings not only results in a substantial distortion from planarity. but the metal center also tends to lie closer to the *ipso*-carbon atoms and therefore the C–C bond opposite the *ipso*-carbon atoms is shortened. Moreover, the angle θ at the bridging atom E is considerably lower than expected for an ideally hybridized atom.

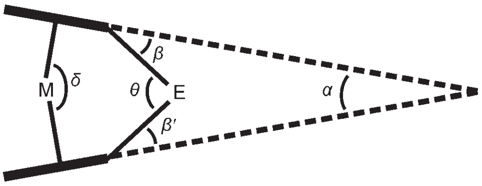


Figure 1. Common set of angles to describe [1]metallocenophanes; for details, see text. E = bridging moiety.

In the UV/Vis spectrum of the strained FCPs, the longer wavelength band is red-shifted and the absorption coefficient of this band increases with the extent of ring tilt. In most cases, in the ^{13}C NMR spectra of the [1]FCPs a remarkably large upfield chemical shift is observed for the *ipso*-carbon atom attached to the bridging atom. This distinguishing feature clearly reflects the structural distortion from a planar geometry imposed by the bridging moiety. Furthermore, the extent of the upfield shift, within one series of similar compounds, can be taken as an indication of the overall ring strain present in the system. Consequently, the release of ring strain through ROP leads to a downfield shift of the *ipso*-carbon signals.

Calculations using density functional theory indicate that the tilt angle α plays a key role in determining the ROP propensity of FCPs.[13] Accordingly, the energy required to tilt the Cp rings is similar to the experimentally determined ΔH_{ROP} value. This implies that the ring tilting is the most considerable factor in determining the thermodynamic tendency of the rings to polymerize. Upon tilting, the frontier orbital energies of metallocenes are increased and the symmetry is reduced from D_{5h} to C_{2v}. Furthermore, the HOMO–LUMO energy gap decreases as the tilt angle increases and is slightly modified by the nature of the bridging element. Dimethylsila[1]ferrocenophane has a low-lying empty orbital, partially located on the *ipso*-carbon atom, which is a possible site for nucleophilic attack during the ROP process.

FCPs with methylated Cp rings have also been polymerized. The tilt angle is 18.6(3)° for the dimethylated species $[(\eta^5\text{-}C_5H_3Me)_2FeSiMe_2]$ and 16.1(3)° for the fully methylated analogue $[(\eta^5\text{-}C_5Me_4)_2FeSiMe_2]$.[14] These values, compared with those of their nonmethylated counterparts, revealed that with increasing ring methylation, the tilt angle decreases significantly. Whereas the onset temperature for the thermal ROP increases by increasing the methylation level, the corresponding enthalpy ΔH_{ROP} is not substantially affected, as revealed by differential scanning calorimetry (DSC) data.[15]

As the d^6 ferrocene unit is relatively reluctant to bend, there is appreciable strain energy in forming the ansa ring. as evidenced by the greater departure from planarity at the *ipso*-carbon atoms. Contrary to FCPs, early-transition-metal ansa metallocenes are thermally more stable and much less prone to rupture at the ansa bridge.[16] Generally, a longer bridge results in a less constrained geometry.

Therefore, whenever a silicon atom is replaced by boron the tilt angle is enlarged, whereas replacement by Ge or Sn results in a smaller tilt angle. Incorporation of a pair of vicinal ansa bridges adds further strain to the molecule, as in the case of bis(disilane)-bridged [2][2]metallocenophanes (M = Fe or Ru). Steric and electronic effects also influence the course of the ROP process. In many cases the thermal ROP was monitored by DSC, thereby allowing the determination of the ROP enthalpy (Table 1) as well as the ROP onset.

In other cases, the melt transition of the monomer (sharp endotherm) is overlapped with the ROP process (broad exotherm), leading to an underestimation of the ΔH_{ROP} value. Many examples of reactive and resistant FCPs towards thermal ROP are presented in Tables 2–6.

Table 1: Strain energies [kJ mol^{-1}] of [1]FCPs.

Ansa bridge	$-\Delta H_{ROP}$	Ansa bridge	$-\Delta H_{ROP}$	Ansa bridge	$-\Delta H_{ROP}$
$SiMe_2$	80	S	130	Sn*t*Bu_2	36
$SiPh_2$	60	Se	110	PPh	68
$B{=}N(SiMe_3)_2$	95	$Sn(Mes)_2$[a]	18	(−)P(bor)[a]	81
(−)P(men)[a]	83				

[a] Mes = 2,4,6-trimethylphenyl, bor = bornyl, men = menthyl.

Table 2: Polymerizable sila[1]ferrocenophanes by thermal ROP.

Ansa bridge	α [°]	Ansa bridge	α [°]
$Si(OMe)_2$	18.6(1)[17]	$Si(C{=}CPh)_2$	19.23(12)[25]
$SiMe_2$	20.8(5)[18]	$SiMe(C{=}CPh)$	20.53(14)[25]
$SiCl_2$	19.2(4)[19]	SiMePh	21.0(2)[26]
$Sifc_2$	20–22[20]	$Si(CH_2)_3$[a]	20.61(8)[27]
SifcMe	21.3[21]	Si(fc)[a]	19.4(2)[27]
SiH_2	19.1(1)[22]	$SiMe(o\text{-}C_6H_4\text{-}CH_2NMe_2)$[b]	21.27(1)[28]
$SiPh_2$	19.2[23]	Si(O*t*Bu)$_2$	20.3[29]
SiMeCl	19.37(32)[24]	$SiMeN\{(CH_2)_3SiMe_2\text{-}(CH_2)_2SiMe_2\}$	21.0(2)[30]

[a] Spirocyclic. [b] Pentacoordinated.

Table 3: Polymerizable FCPs by thermal ROP.

Ansa compound	α [°]
$[Fe(\eta^5\text{-}C_5H_4)_2CH_2CH_2]$	21.6(4)[31]
$[Fe(\eta^5\text{-}C_5H_4)_2Se]$	26.4(2)[32]
$[Fe(\eta^5\text{-}C_5H_4)_2S]$	31.05(10)[33]
$[Fe(\eta^5\text{-}C_5H_4)_2B{=}N\mathit{i}Pr_2]$	31.0(2) and 31.4(2)[a] [33]
$[Fe(\eta^5\text{-}C_5H_4)_2B{=}N(SiMe_3)_2]$	32.4(2)[b] [34]
$[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5Me_4)CH_2PPh]$	14.8(3) and 15.0(4)[a] [35]
$[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5Me_4)CH_2PMes]$	18.1(2) and 18.3(2)[a] [35]
$[Fe(\eta^5\text{-}C_5H_3\mathit{t}Bu)_2SiPh_2]$	18.81[36]
$[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5Me_4)CH_2S]$	18.5(1)[35]

[a] Two independent molecules in the unit cell. [b] The largest value in the literature.

Table 4: Polymerizable Ge- and Sn-bridged FCPs by ROP.

Ansa bridge	α [°]
GePhCl	18.4[37]
$GeMe_2$	19.0(9)[38]
$GePh_2$	16.6[39]
$GeMe_2GeMe_2$	3.94[a] [40]
$Sn(C_6H_2\mathit{i}Pr_3)_2$	14.7[41]
$Sn\mathit{t}Bu_2$	14.1(2)[42]
$SnMes_2$	14.5(2), 15.3(2), and 15.7(3)[b] [43]

[a] The digermanium-bridged compound has a smaller tilt angle than the CH_2CH_2- and $SiMe_3SiMe_3$-bridged FCPs, as expected. It is resistant against both thermal and anionic ROP. Under mild conditions in the presence of Pd^{II} or Pt^{II} complexes, the Ge–Ge bond undergoes a facile oxidative addition reaction, yielding high-moleculare-weight polymers in good yields. In this case the ROP process is mainly entropically driven, because as the monomer is incorporated to the macromolecular chain, the degrees of freedom are increased, similarly to the ROP of octamethylcyclotetrasiloxane. [b] Three independent molecules in the unit cell.

Table 5: FCPs resistant against thermal ROP.

Ansa compound	α [°]
$[Fe(\eta^5\text{-}C_5H_4)_2SiMe_2fcSiMe_2]$	4.9(3)[44]
$[Fe(\eta^5\text{-}C_5H_4)_2SiMe_2SiMe_2]$	4.19(2)[18]
$[Fe(\eta^5\text{-}C_5H_4)_2SiR_2OSiR_2]$, R = Me or Ph	2.5(12)[45]
$[Fe(\eta^5\text{-}C_5H_4)_2SiMe_2(OSiMe_2)_x]$, $x = 2$ or 3	1.5(5)[45]
$[Fe(\eta^5\text{-}C_5H_4)_2Pt(PEt_3)_2SiMe_2]$	11.6(3)[47]
$[Fe(\eta^5\text{-}C_5H_3SiMe_3)_2SiMe_2SiMe_2]$[a]	5.9(6)[48]
$[Fe(\eta^5\text{-}C_5H_4)_2Ge(C_4Me_4)]$	18.9[51]
$[(SiMe_2SiMe_2)_2Fe(\eta^5\text{-}C_5H_3)_2]$	7.2(3)[b] [46]
$[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5Me_4)CH_2P(Ph)(Me)]^+CF_3SO_3^-$	11.4(7)[58]
$[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5Me_4)CH_2SiMe_2]$	11.8(1)[58]
rac-$[Fe(\eta^5\text{-}C_9Me_6)_2SiMe_2]$	13.0 and 13.8[c] [49]
$[Fe(\eta^5\text{-}C_5H_4)_2Si(OC_6H_4\text{-}\mathit{p}\text{-}NO_2)_2]$	18.6(2)[d] [36]
$[Fe(\eta^5\text{-}C_9Me_6)(\eta^5\text{-}C_5H_4)SiMe_2]$	17.2[50]
$[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5Me_4)CH_2GePh_2]$	11.81(5)[52]
$[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5Me_4)CH_2GeMe_2]$	10.99(2)[52]
$[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5Me_4)CH_2Sn\mathit{t}Bu_2]$	6.64(2)[52]
$[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5Me_4)CH_2SnMes_2]$	7.1(1)[52]
$[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5Me_4)CH_2SnMe_2]$	7.5(1)[52]
$[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5Me_4)CH_2ZrCp_2]$	−5.5(2)[e] [53]

[a] Incorporation of one sterically demanding $SiMe_3$ group per Cp ring increases the tilt angle. [b] Even the more strained bis(disilane)-bridged on adjacent positions [2][2]FCP is resistant. [c] Two independent molecules in the unit cell. [d] The nitro and the hexamethylindenyl derivatives are decomposed at elevated temperatures. Attempts to polymerize $[Fe(\eta^5\text{-}C_9Me_6)(\eta^5\text{-}C_5H_4)SiMe_2]$ with $PtCl_2$ (C_6D_6, RT) were also unsuccessful. [e] The negative value denotes tilting away from the C–Zr bridge.

Table 6: Metallized sila[1]ferrocenophanes that are resistant against ROP.

Ansa bridge	α [°]
$SiMe\{Co_2(CO)_6C_2Ph\}$	19.09(21)[54]
$SiMe\{Co_2(CO)_6C_2\mathit{n}Bu\}$	19.51(19)[54]
$Si\{Co_2(CO)_6C_2\mathit{n}Bu\}_2$	19.87(22)[54]
$SiMe\{Mo_2Cp_2(CO)_4C_2Ph\}$	20.93(20)[54]
$SiMeCo(CO)_4$	19.98(5)[55]
$SiMe\{Ni_2(Cp)_2C_2Ph\}$	21.21(21)[56]
$SiMe\{Ni(dppe)C_2Ph\}$[a]	20.38(10)[54]
$SiMe\{Ni(dmpe)C_2Ph\}$[a]	19.90(13)[54]

[a] dmpe = 1,2-bis(dimethylphosphino)ethane. [b] dppe = 1,2-bis(diphenylphosphino)ethane.

Highly metallized sila[1]ferrocenophanes, although they possess large tilt angles, are resistant against ROP, either thermally or transition-metal-catalyzed, possibly owing to sterical hindrance. Moreover, attempted anionic ROP with BuLi caused declusterization. Several examples of phosphorous-bridged [1]FCPs are presented in Table 7. The phosphonium-bridged derivative $[Fe(\eta^5\text{-}C_5H_4)_2P(Ph)(Me)]^+\text{-}(OSO_2CF_3)^-$ possesses a tilt angle of 24.4(5)° and undergoes both thermal and $PtCl_2$-catalyzed ROP.[57] Thermal ROP was also accomplished for the chiral (−)menthylphospha- and (−)bornylphospha-bridged [1]FCPs. The former complex possesses a large tilt angle ($\alpha = 27.43°$).[58] Ruthenocenophanes possess greater tilt angles than the analogous iron species, owing to the larger size of the Ru atom (Table 8).

Table 7: Polymerizable phosphaferrocenophanes by thermal ROP.

Ansa compound	α [°]
$[Fe(\eta^5\text{-}C_5H_4)_2PPh]$	27.0(1)[59]
$[Fe[\eta^5\text{-}C_5H_3(SiMe_3)]_2PPh]$	27.5(6)[a] [60]
$[Fe[\eta^5\text{-}C_5H_3(SiMe_3)]_2P(S)Ph]$	25.3(3)[60]
$[Fe(\eta^5\text{-}C_5H_4)_2P(\mathit{p}\text{-}C_6H_4\text{-}\mathit{t}Bu)]$	26.9(3)[61]
$[Fe(\eta^5\text{-}C_5H_4)_2P(Ph)\cdot BH_3]$	24.38(10)[62]
$[Fe(\eta^5\text{-}C_5H_4)_2P(Ph)\cdot BCl_3]$	25.01(4)[62]

[a] Attachment of the sterically demanding $SiMe_3$ substituents to the Cp rings introduces further strain, as in the case of the $SiMe_2SiMe_2$ bridge.

Attempted transition-metal-catalyzed ROP of (on adjacent positions) silicon-bridged [1][1]zirconocenophanes $[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2Zr(NEt_2)_2]$ and $[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2ZrCl_2]$ were both unsuccessful.[66] Contrary to ferro-

Table 8: ROP behavior of ruthenocenophanes.

Ansa compound	α [°][a]	ROP behavior
$[Ru(\eta^5\text{-}C_5H_4)_2SiMe_2SiMe_2]$	7.8(5) [+3.6][63]	unreactive
$[(SiMe_2SiMe_2)_2Ru(\eta^5\text{-}C_5H_3)_2]$	12.9(2) [+5.7][63]	unreactive
$[Ru(\eta^5\text{-}C_5H_4)_2CH_2CH_2]$	29.6(5) [+8.0][64]	reactive
$[Ru(\eta^5\text{-}C_5H_4)_2Zr(C_5H_4\mathit{t}Bu)_2]$	10.4 [+4.4][65]	unreactive
$[Ru(\eta^5\text{-}C_5H_4)_2SnMes_2]$	20.9(3), 20.2(3), and 20.8(4)[b] [+5.5][65]	reactive

[a] The value in the brackets denotes the deviation from the FCP counterpart. [b] Three independent molecules in the unit cell.

cene compounds, zirconocene complexes are bent inherently, and therefore the effective tilt angle α' (i.e. the deviation from the nonbridged bent analogues) is used to describe their structure. The effective tilt angles for the above compounds are 18.9° and 15.4°, respectively. Attempts to induce anionic or thermal ROP to the germolyl compound [Fe(η^5-GeC$_4$H$_4$)$_2$Si(SiMe$_3$)$_2$] also failed.[67]

Carbon-bridged FCPs have been polymerized by transition-metal-catalyzed ring-opening metathesis polymerization (ROMP). From the tilt angle values (Table 9), it is noteworthy that even when Cp rings are virtually planar and parallel to each other, as in the case of the C(*t*Bu)=CH-CH=CH bridge, ROMP occurs. The driving force in such cases is the substantial bond angle strain in the bridge, arising from the steric bulk of the bridging moieties.

Table 9: Polymerizable FCPs by ROMP.

Ansa bridge	Tilt angle α [°]
CH=CH	22.6[68]
C(OMe)=CH−CH=CH	7.16 and 11.07[a] [69]
CH=CH−CH=CH	6.7[69]
C(*t*Bu)=CH−CH=CH	≈0[70]
C(Ph)=CH−CH=CH	8.2[71]
C(Mes)=CH−CH=CH	10.2[71]
CH=CH−CH$_2$	11.3[72]

[a] Two independent molecules in the unit cell.

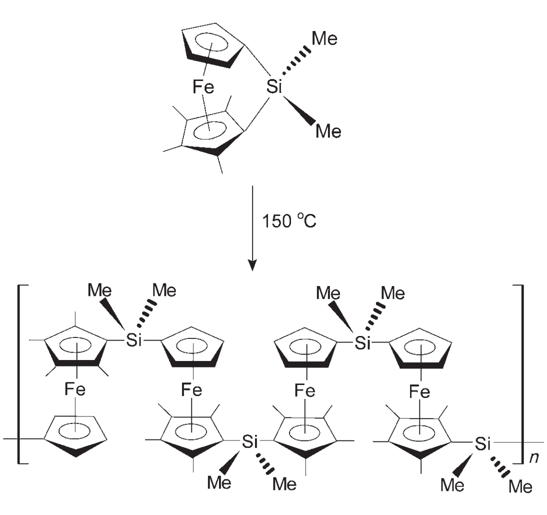
As already mentioned, Rauchfuss and co-workers utilized the desulfurizing activity of *n*Bu$_3$P to polymerize [(η^5-C$_5$H$_3$R)$_2$FeS$_3$] (R = *t*Bu or H), producing poly(ferrocenylene persulfides). NMR analysis of the product obtained by ROP of the corresponding S-Se-S-bridged derivative revealed that selenium is abstracted. Therefore, the ROP mechanism is based on the abstraction of the central atom of the bridge and does not rely on strain release.[73] Using the same concept, polymeric networks were formed from the bis(trithia)bridged [3][3]FCPs.[74] Finally, deselenization of [*n*BufcSe$_3$] gave polymers with moderate molecular weight and high polydispersity.[75]

Except for the relatively numerous reports about the ROP behavior of metallocenophanes, there are limited studies dealing with related ansa complexes. A remarkable example is the ROP behavior of the dimethylsila[1]chromarenophane, which exhibits a tilt angle of 16.6(3)°.[76] Whereas this monomer has no tendency to undergo either thermal or anionic ROP, it can be copolymerized by both methods with [fcSiMe$_2$] to produce low-molecular-weight random heterobimetallic copolymers, in which the chromarenophane incorporation does not exceed 38 %. The inability of this monomer to undergo thermal ROP was attributed to the low Cr–arene bond energy, as evidenced by the exclusive formation of Cr mirror at elevated temperatures. Attempted thermal ROP of bora[1]chromarenophane also resulted in decomposition and deposition of chromium metal.[77] Facile transition-metal-catalyzed ROP of the SiRR′-bridged (R = Me, R′ = Me or Et) chromarenophane was achieved in the presence of Karstedt's catalyst at ambient temperature.[76b] Recently, preliminary experiments revealed that [{(η^6-C$_6$H$_5$)Mn(η^5-C$_5$H$_4$)}Si*i*Pr$_2$] ($\alpha = 16.97°$) undergoes ROP.[78]

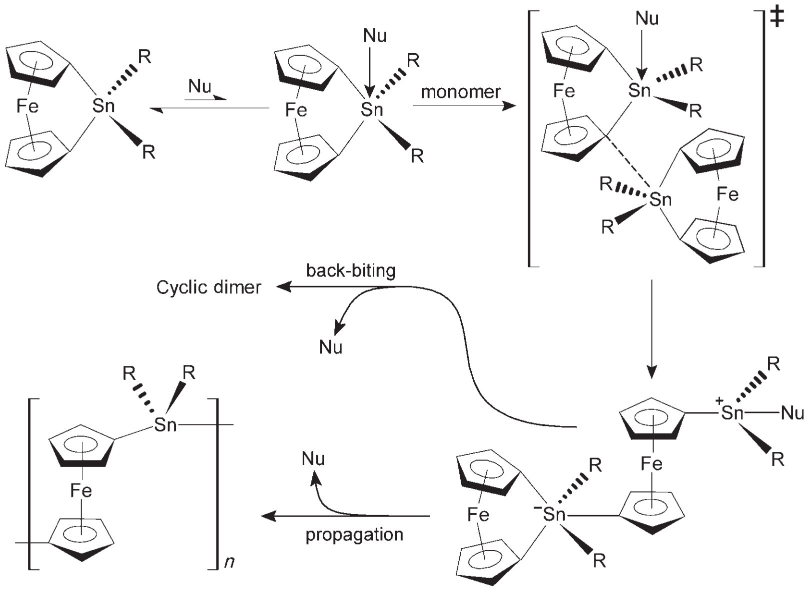
Ansa-cycloheptatrienyl–cyclopentadienyl complexes have also been examined. The diphenylsila[1]trovacenophane [{(η^7-C$_7$H$_6$)V(η^5-C$_5$H$_4$)}SiPh$_2$] is strained ($\alpha = 17.3°$), but is relatively thermally robust, thereby failing to be polymerized.[79] A DSC study of the [{(η^7-C$_7$H$_6$)Ti(η^5-C$_5$H$_4$)}SiMe$_2$] ($\alpha = 24.1°$) indicated the formation of irregular poly(troticenyldimethylsilane), which includes all possible Cp-Si-Cp, Cht-Si-Cht, and Cp-Si-Cht linkages (Cht = cycloheptatrienyl).[80] Contrary to the thermally induced ROP, regioregular oligomerization was achieved in the presence of a catalytic amount of the [Pt(PEt$_3$)$_2$SiMe$_2$]-bridged troticenophane, resulting in a structure with exclusively Cp-Si-Cht sequences.[81] The dimethylsila[1]trochrocenophane [{(η^7-C$_7$H$_6$)Cr(η^5-C$_5$H$_4$)}SiMe$_2$] ($\alpha = 15.6°$) undergoes ROP in the presence of Karstedt's catalyst, yielding low-molecular-weight polymers with high conversions.[82] Attempted copolymerization with either dimethyl- or methylphenylsila[1]ferrocenophane yielded the corresponding PFS homopolymers. Attempted photolytic ROP was also unsuccessful.

2.3. ROP Methodologies

Thermal ROP at elevated temperatures either in solution or in bulk (melt) affords high-molecular-weight polymers with broad polydispersity indices. Owing to its relatively high tolerance towards functional groups, a wide range of strained monomers have been used. To gain insight into the mechanism of the thermal ROP of silicon-bridged [1]FCPs, Pudelski et al. polymerized monomers bearing unsymmetrically methylated Cp rings.[83] The reaction proceeds through a nonselective cleavage of Si−Cp$^{\mathrm{H}}$ and Si−Cp$^{\mathrm{Me}}$ bonds as evidenced by ^{1}H NMR microstructure analysis, cyclic voltammetry, as well as ESR data on the oxidized product (Scheme 5). The nature of the propagating species is not known with certainty. A carbanionic mechanism is ruled out completely, because the ROP of monomers bearing chlorosilyl groups results in high-molecular-weight polymers. Intri-



Scheme 5. Synthesis of amorphous PFS by thermal ROP.



Scheme 6. Nucleophile-assisted ROP of tin-bridged [1]FCPs at ambient temperature.

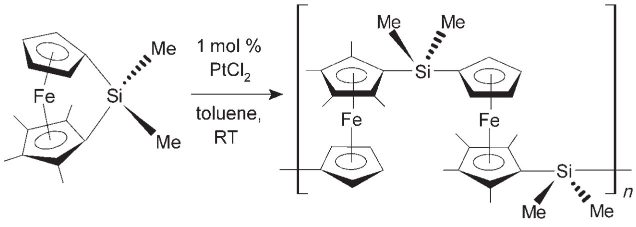
guingly, the thermal ROP of monomers bearing chloropropyl groups gives moderate-molecular-weight polymers. Since such groups are well-known chain-transfer agents, a mechanistic process involving radicals should not be dismissed. Nevertheless, more studies are needed to elucidate the thermal ROP mechanism.

A heterolytic mechanism involving initiation by trace quantities of nucleophilic impurities was proposed in the case of the solution ROP of tin-bridged [1]FCPs (Scheme 6).[84] Noticeably, the ROP process is dramatically accelerated upon addition of amine nucleophiles. The dimethylgermyl- and dichlorosilyl-bridged analogues also undergo ROP in the presence of pyridine, whereas the dimethylsilyl counterpart is resistant. The rate of the ROP process relies on the stabilization of the pentacoordinated intermediate, which is strongly affected by steric effects and the electrophilicity of the bridging atom.

The first report of living carbanionic ROP appeared in 1994, and this process permitted the synthesis of PFS with predictable molecular weights and narrow molecular-weight distributions.[85] Since thermal ROP is unable to produce materials with a high degree of molecular and compositional homogeneity, living carbanionic ROP is of high value here. Importantly, this methodology provided access to a wide variety of novel copolymers with well-defined structures and architectures, provided that only functionalities that are inert toward carbanions are present at the monomer. However, an exhaustive purification of reagents is required to avoid premature termination. The mechanism is based on a Cp–Si bond cleavage, as evidenced by the structure of the oligomers, prepared by either ferrocenyllithium- or dilithioferrocene-initiated ROP.[86]

In 1995 two groups independently described the transition-metal-catalyzed ROP of sila- and germaferrocenophanes.[87] Various platinum (Pt^0, Pt^{II}), palladium (Pd^0, Pd^{II}), and rhodium (Rh^I) complexes catalyze the ROP in solution at room temperature to yield high-molecular-weight polymers. Compared to living carbanionic ROP, this convenient approach does not require extremely high purity levels. Contrary to thermal ROP, where in many cases high polymerization temperatures are needed, the transition-metal-catalyzed ROP occurs under mild conditions, rendering many monomers reactive which otherwise decomposed upon attempted thermal ROP. Using this route, a crystalline material with a regioregular microstructure was produced from the corresponding FCP with different levels of methylation at the Cp rings, contrary to the amorphous polymers obtained from thermal ROP. In this case, ROP proceeds exclusively by a selective $Si-Cp^H$ bond-cleavage mechanism, because the $Si-Cp^{Me}$ bond is resistant against $PtCl_2$-catalyzed ROP, as concluded from the failure of $[(\eta^5\text{-}C_5Me_4)_2FeSiMe_2]$ to undergo ROP under these conditions (Scheme 7).[88]

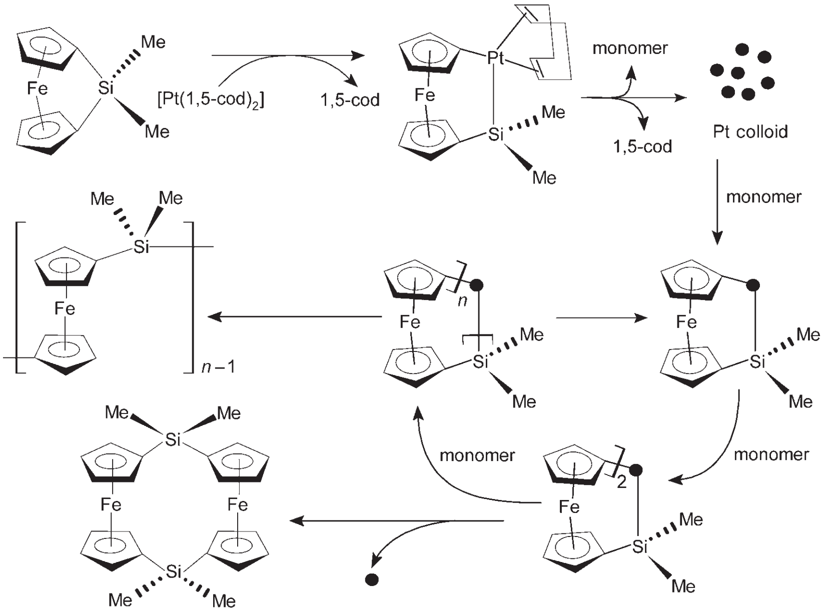
Phosphorus(III)-bridged [1]FCPs are resistant against transition-metal-catalyzed ROP, presumably owing to the ligation of the phosphorous lone pair to the catalyst's metal center. Up to now, there is no successful organolithium-initiated or transition-metal-catalyzed ROP of tin-bridged [1]FCPs.



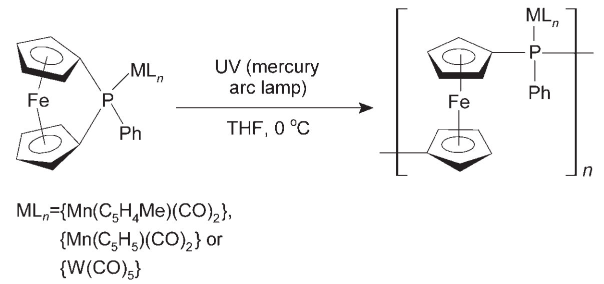
Scheme 7. Synthesis of regioregular PFS by $PtCl_2$-catalyzed ROP.

Transition-metal-catalyzed ROP was initially believed to proceed through homogeneous reactions.[89] Subsequent studies suggested a heterogeneous catalytic route with colloidal metal as the main active catalyst (Scheme 8).[90] The generated platinasila[2]ferrocenophane acts as a precatalyst. The heterogeneous mechanism was supported by end-group analysis of the isolated $[\{Fe(\eta^5\text{-}C_5H_4)_2SiMePh\}_n]$ polymer, revealing that the dimethylsilylferrocenophane component of the precatalyst does not incorporate into the growing polymer. This observation was additionally confirmed by using $[Fe(\eta^5\text{-}C_5H_4)_2Pt(1,5\text{-cod})Sn\textit{t}Bu_2]$ as a precatalyst. Moreover, significant retardation of the reaction was observed in the presence of mercury, a well-known inhibitor for heterogeneous reactions. Since no inhibitors for homogenous reactions were checked to find out whether a relevant retardation occurs or not, the coexistence of homogeneous catalytic reactions should not be ruled out.

In 2000 the first photolytic ROP was published.[91] The monomers that were used were the phosphorous-bridged [1]FCPs coordinating to an organometallic fragment: $[Fe(\eta^5\text{-}C_5H_4)_2P(Ph)X]$ ($X = \{Mn(\eta^5\text{-}C_5H_5)(CO)_2\}$, $\{Mn(\eta^5\text{-}C_5H_4Me)(CO)_2\}$, or $\{W(CO)_5\}$; Scheme 9). The monomer $[Fe(\eta^5\text{-}C_5H_4)_2P(Ph)W(CO)_5]$ possesses a tilt angle of 25.6°. Since the $^{31}P\{^1H\}$ NMR spectrum of the produced polymer



Scheme 8. Proposed mechanism for the transition-metal-catalyzed ROP of [fcSiMe$_2$]; cod = cyclooctadiene.

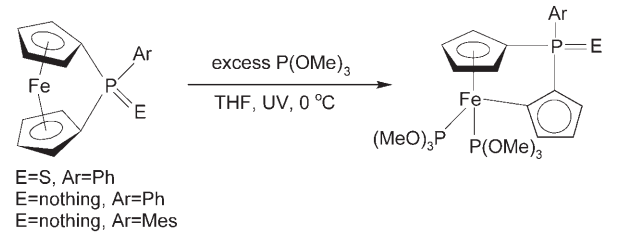


Scheme 9. ROP of phospha[1]ferrocenophanes under broad-band UV illumination.

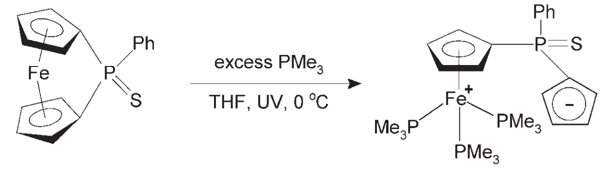
showed only a sharp signal, the ROP process is completely regioselective. Nonchlorinated donor solvents (THF, acetonitrile) promote the regioselectivity, whereas apolar and chlorinated ones give rise to complicated ^{31}P{^{1}H} NMR spectra. This is the only report in which a metallized FCP undergoes ROP. An appreciable advantage of this methodology is the well-defined structure of the final polymer, because the pendant group is present in every repeating unit. Other strategies, in which the organometallic fragments are introduced through side-chain functionalization reactions of polymers, suffer from incomplete incorporation of the metallic moieties.[56] Thermal and transition-metal-catalyzed ROP of the metallized monomers were both unsuccessful. Catalytic amounts of *n*BuLi induced anionic ROP to the Mn derivatives, while a relevant experiment was not attempted in the case of the W compound.

To elucidate the photolytic ROP mechanism, various phospha[1]ferrocenophanes were irradiated with UV light in the presence of a large excess of P(OMe)$_3$ (Scheme 10).[92] The molecular structure of the product was determined by X-ray crystallography and revealed an η^5→η^1 haptotropic shift. Heating of this intermediate gave a polymer, signifying that it indeed possesses structural characteristics requisite for ROP. Replacement of P(OMe)$_3$ by the stronger-coordinating agent PMe$_3$ revealed that the η^1-Cp ring dissociates completely from the iron center and is bonded to phosphorous (Scheme 11).

These results support a mechanism in which reactive intermediates are initially formed and afterwards react with the remaining monomer, thereby propagating the ROP (Scheme 12). Recently, it was found that the photolytically induced haptotropic shifts are reversible upon heating.[93] These encouraging results promted investigation of the photolytic living carbanionic ROP of [fcSiMe$_2$].[94] Preliminary experiments revealed that neither (C_5H_4Me)Li nor UV broad-band irradiation ($\lambda > 300$ nm) alone causes a ring-opening reaction to this monomer. However, the monomer reacts with (C_5H_4R)Li (R = Me or H) in the presence of UV light by a Fe–Cp bond-cleavage mechanism (Scheme 13).

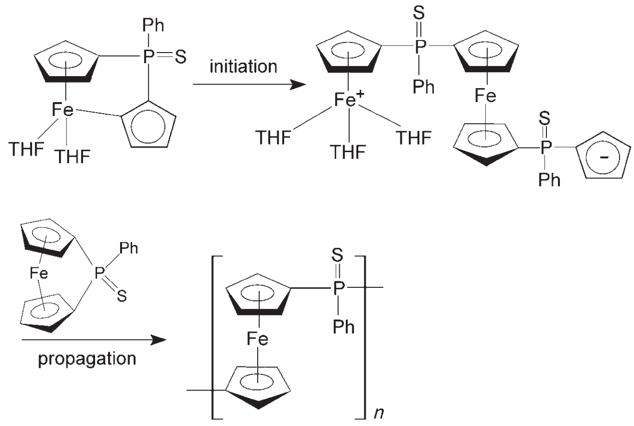


Scheme 10. Photolysis of FCPs in the presence of P(OMe)$_3$.

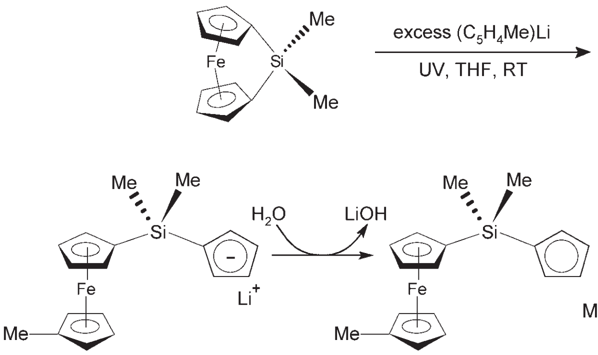


Scheme 11. Photolysis of FCPs in the presence of PMe$_3$.

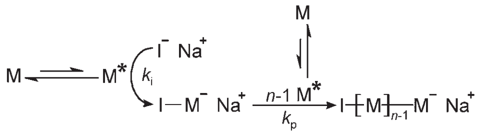
The UV photoirradiation further weakens the already relatively weak Fe–Cp bond of the highly strained [fcSiMe$_2$] complex, thus facilitating the nucleophilic attack at the iron center. Under the same conditions, using higher monomer loadings, low-molecular-weight polymers were formed with polydispersities ranging from 1.18 to 1.35. However, living photolytic carbanionic ROP was achieved using (C_5H_5)Na as an initiator. Kinetic studies revealed retardation with increasing temperature, thus providing mechanistic insight (Scheme 14).[95] Upon irradiation some monomers (M) are promoted to a photoexcited state (M*). The photoexcited monomer M*, which is potentially solvated, then reacts with the initiator (I, with rate constant k_i) to form a ring-opened



Scheme 12. Proposed mechanism for the photolytic ROP of phospha[1]ferrocenophanes.



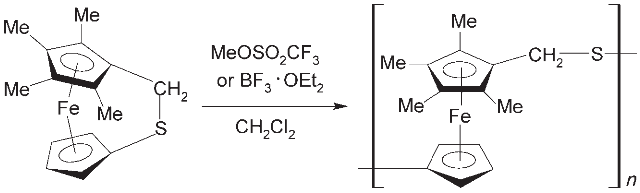
Scheme 13. Ring-opening reaction of [fcSiMe$_2$] upon UV photoirradiation.



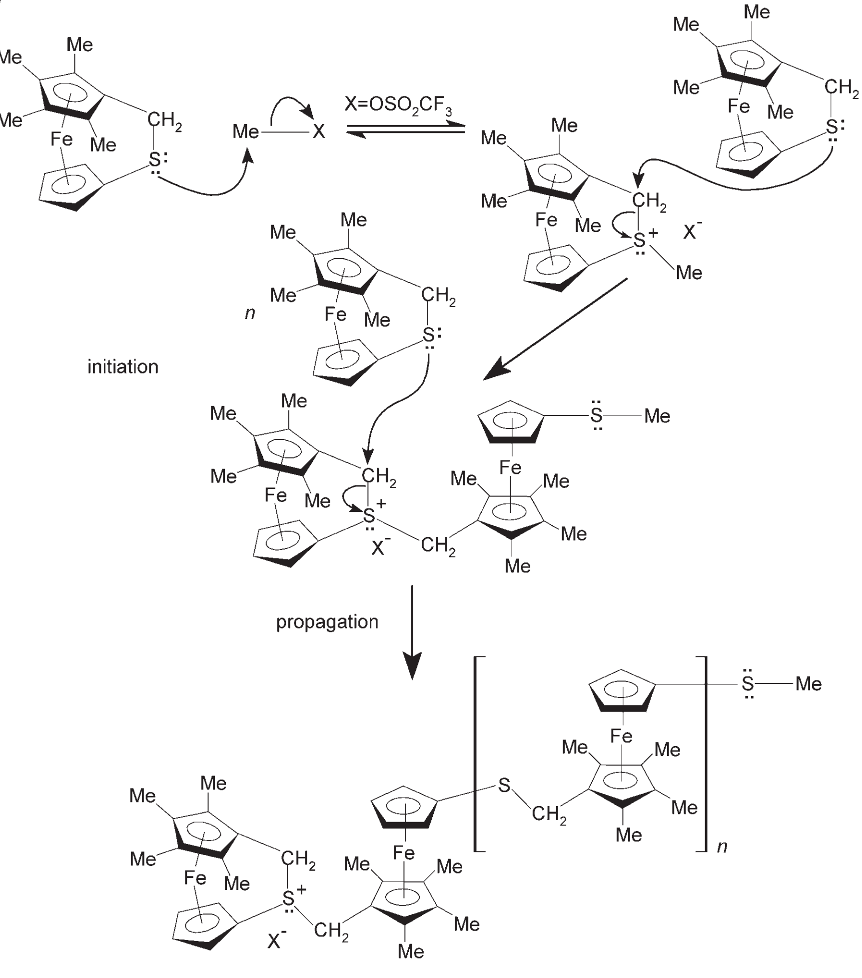
Scheme 14. Proposed mechanism for photolytic living ROP; M = monomer, I = initiator.

adduct, which in turn undergoes chain propagation (with rate constant k_p) in the presence of the M* monomer. At higher temperatures, the equilibrium between M and M* is expected to lie in favor of the ground-state monomer, thus negatively affecting the ROP process.

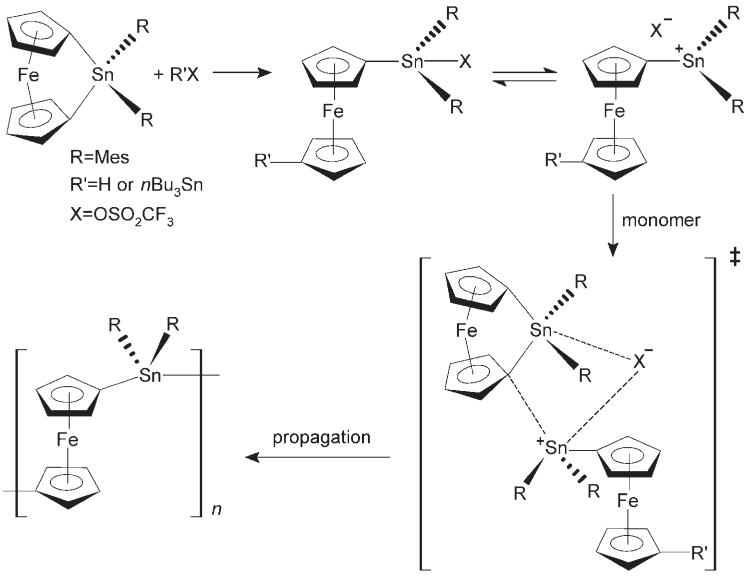
The first cationic ROP of a metal-containing ring appeared in 1998 and involved the polymerization of a strained carbathio[2]ferrocenophane (Scheme 15).[96] The proposed mechanism is illustrated in Scheme 16. The cationic ROP of stanna[1]ferrocenophane was explained on the basis of the mechanism presented at Scheme 17.[97] Recently, the cationic ROP of a cyclic pentacoordinated sila[1]ferrocenophane was described (Scheme 18).[98] Solid-state ROP of symmetrically substituted sila[1]ferrocenophanes upon ^{60}Co γ irradiation yields high-molecular-weight polymers with properties similar to the materials prepared by thermal ROP.[99] However, thermal ROP of unsymmetrically substituted monomers generates amorphous polymers, whereas the γ-ray-induced ROP forms stereoregular materials.



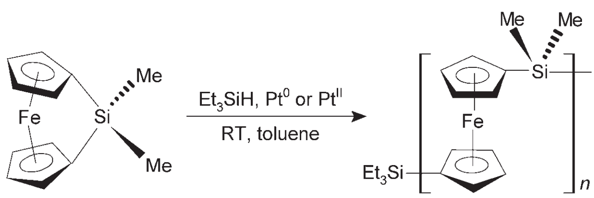
Scheme 15. Cationic ROP of carbathio[2]ferrocenophane.



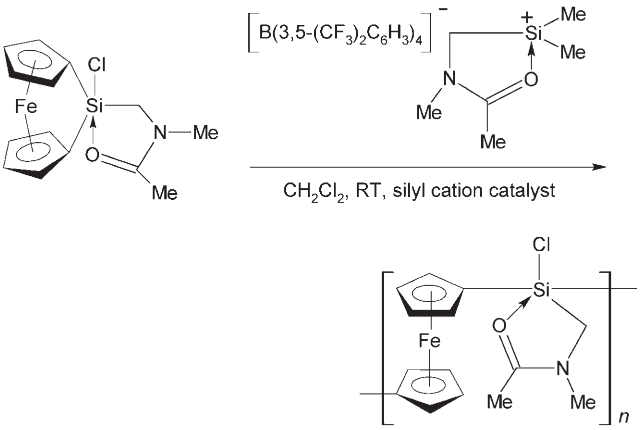
Scheme 16. Proposed mechanism of the cationic ROP of carbathio[2]ferrocenophane.



Scheme 17. Proposed mechanism of the cationic ROP of stanna[1]ferrocenophanes.



Scheme 19. Controlled synthesis of PFS by Pt-catalyzed ROP in the presence of Et_3SiH.



Scheme 18. Cationic ROP of sila[1]ferrocenophanes.

3. Synthesis of Copolymers—Macromolecular Architectures

Random copolymers were prepared by the thermal ring-opening copolymerization of [$fcSiMe_2$] with cyclotetrasilanes,[100] and dialkylgerma[1]ferrocenophanes.[101] Both thermal and $PtCl_2$-catalyzed copolymerization of [$fcGeMe_2$] and [$fcSiMe_2$] yielded copolymers with a monomodal molecular-weight distribution.[102] Transition-metal-catalyzed copolymerization of [$fcSiMe_2$] with either benzosilacyclobutane or tetramethyldisilacyclobutane led to the formation of random copolymers. In all cases, the copolymer composition was identical to the initial feed ratio. Thermal copolymerization at 150 °C resulted in FCP-rich materials.[103] Later on, similar copolymers were obtained by [Rh(1,5-cod)$_2$] OTf-catalyzed copolymerization.[104]

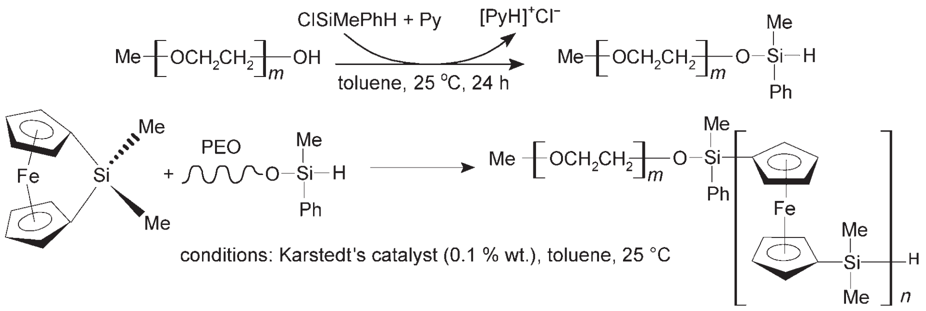
Transition-metal-catalyzed ROP in the presence of varying amounts of Et_3SiH allows convenient control of the molecular weight over the range $M_n = 2000–45\,000$, with polydispersity index values in the range of 1.1–2.3 (Scheme 19).[105] The observed M_n value is greater than expected from the feed ratio of monomer/Et_3SiH, implying that [$fcSiMe_2$] is more reactive towards the catalytic metal center compared to Et_3SiH. Apparently, oxidative addition of the Si–H functionality to the catalytic species competes with the addition of the strained Si–Cp bond of the monomer. During the propagation the concentration of the monomer decreases and Et_3SiH effectively is added to the growing metallomacrocycle, thereby acting as a terminating agent to afford the telechelic polymer. Later on, functionalized silanes were found to be more reactive as capping agents than Et_3SiH, allowing molecular-weight control in the low-molecular-weight range.[106] The reactivity seems to be dependent on the electronegativity and steric demand of the silicon substituents.

This methodology was attempted to extend to other Si–H substrates, giving access to the synthesis of copolymers with block, graft, and star architectures. However, this protocol needs further optimization in order to achieve grafting of polymeric chains rather than the short ones reported so far. Cyclic PFS has been also reported to be available through the transition-metal-catalyzed ROP of [$fcSiMe_2$] in the presence of $BH_3 \cdot THF$ as a cocatalyst.[107]

3.1. Block Copolymers

The first block copolymer was synthesized in 1994 by sequential living anionic ROP of [$fcSiMe_2$] and hexamethylcyclotrisiloxane.[108] Later on, this approach was exploited to the synthesis of various co- and terpolymers.[109] For example, PDMS-*b*-PFS-*b*-PS-*b*-PFS-*b*-PDMS was prepared using a difunctional initiator, whereas PS-*b*-PFS-*b*-PDMS-*b*-PFS-*b*-PS through coupling with Me_2SiCl_2 (PDMS = poly(dimethylsiloxane), PS = polystyrene).

The synthesis of a water-soluble amphiphilic organometallic block copolymer was accomplished starting from a hydroxyl-telechelic poly(ethylene oxide) (PEO).[110] The first step involves the incorporation of the terminal Si–H group through a condensation reaction between the ω-hydroxyl precursor and methylphenylchlorosilane (Scheme 20). Treatment of the ω-hydrosilyl PEO with [$fcSiMe_2$] in the presence of Karstedt's catalyst afforded the diblock copolymer. An amphiphilic metallo-supramolecular copolymer PFS-*b*-PEO



Scheme 20. Synthesis of PEO-*b*-PFS.

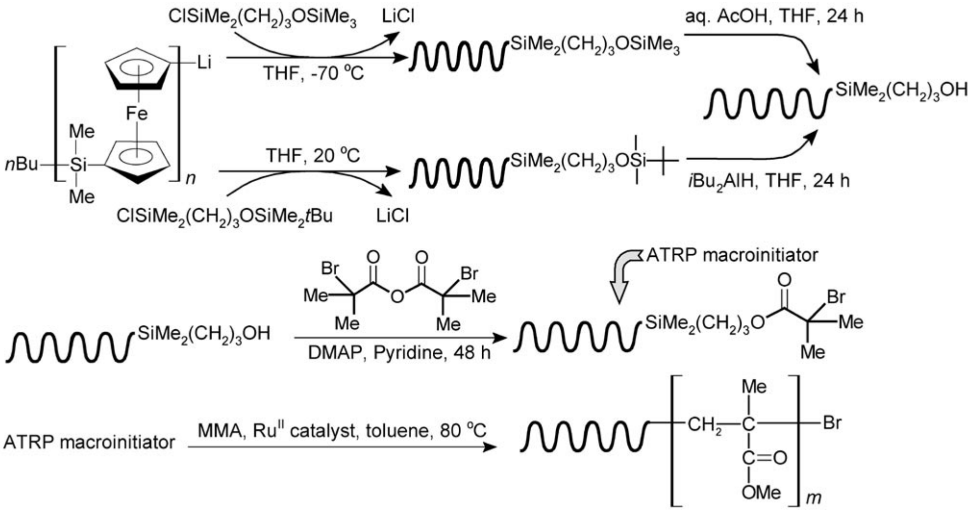
was also prepared by a multistep methodology based on terpyridine chemistry.[111]

A two-step approach was used for the synthesis of oligoferrocenylsilane-*b*-poly[2-(*N*,*N*-dimethylamino)ethyl methacry-late] (Scheme 21).[112] Initially, the anionic ROP of [fcSiMe$_2$] took place in the presence of (*tert*-butyldimethylsilyloxy)-1-propyllithium. The hydroxyl functionality was formed upon hydrolysis of the protective group by nBu$_4$N$^+$F$^-$. Subsequent treatment with potassium hydride generated a living chain end, suitable to commence the anionic polymerization of the methacrylic monomer.

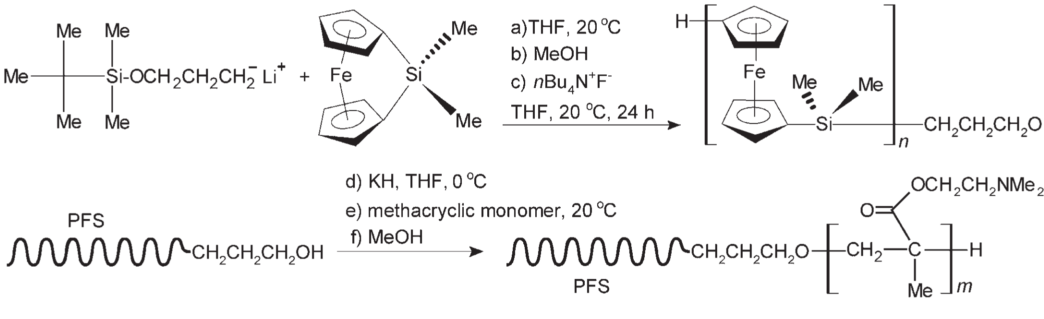
High-molecular-weight asymmetric PFS-*b*-poly(methyl methacrylate) was prepared by combining living anionic ROP and atom-transfer radical polymerization (ATRP) (Scheme 22).[113] In the first step, Me$_3$SiO- or tBu-Me$_2$SiO-functionalized PFS was synthesized by end-capping the living precursors with functional chlorosilanes. In the former case the end-capping was performed at low temperature, thereby avoiding nucleophilic attack of the living chains at the trimethylsilyl ether moieties. Afterwards, the labile protecting groups were hydrolyzed under relatively mild conditions to prevent chain scission of the PFS block. On the other hand, attempted deprotection by nBu$_4$N$^+$F$^-$ was accompanied by partial degradation. Subsequent acetylation with 2-bromoisobutyric anhydride generated the ATRP macroinitiators, which then polymerized MMA in the presence of a ruthenium-based catalyst, affording the diblock copolymers.

A novel heteroarm star copolymer, (PFS)(PI)$_3$, was synthesized using controlled chlorosilane-linking chemistry (Scheme 23).[114] In the first step, a dilute solution of the living PFS block is added dropwise to a huge excess of tetrachlorosilane to ensure that only one polymeric chain is selectively grafted onto the coupling agent. Subsequent to quantitative removal of the SiCl$_4$ excess, the trichlorosilyl-terminated precursor was treated with an excess of polyisoprenyllithium, resulting in complete substitution of the remaining chlorine atoms.

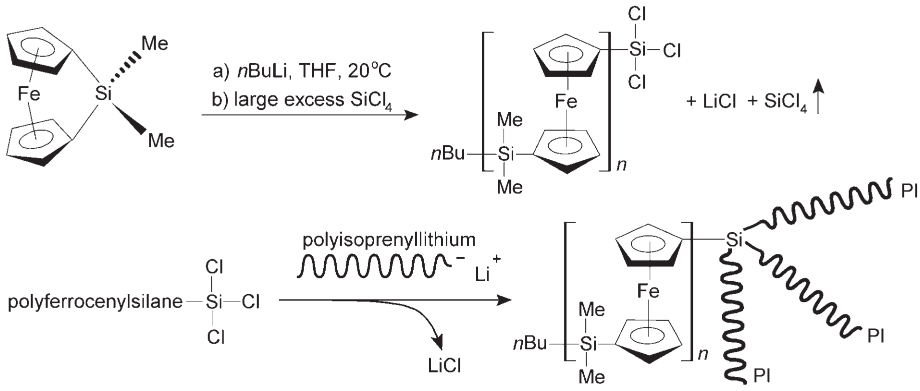
A two-step methodology was utilized for the synthesis of PFS-*b*-poly(γ-benzyl-L-glutamate) (Scheme 24). Initially, treatment of living PFS chains with a fivefold excess of 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane at low temperature and subsequent precipitation in



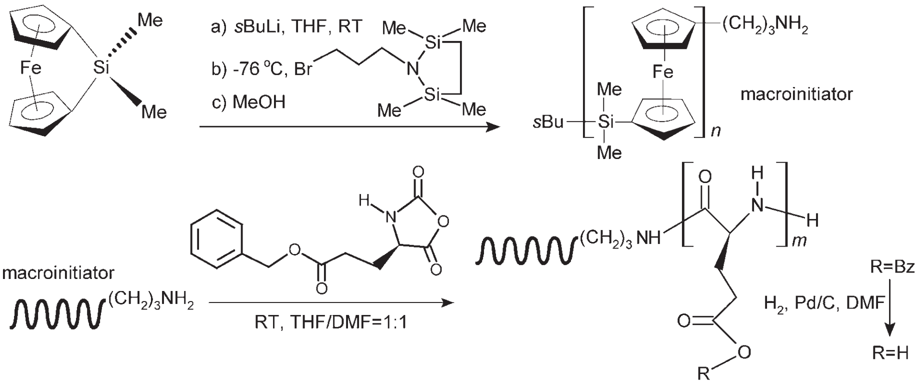
Scheme 22. Synthesis of PFS-*b*-PMMA; MMA = methyl methacrylate, DMAP = 4-(dimethylamino)pyridine.



Scheme 21. Synthesis of oligoferrocenylsilane-*b*-poly[2-(*N*,*N*-dimethylamino)ethyl methacrylate].



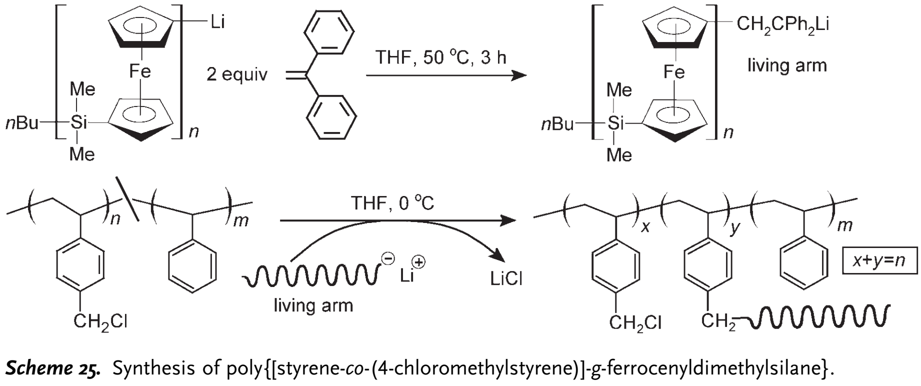
Scheme 23. Synthesis of a heteroarm star copolymer; PI = polyisoprene.



Scheme 24. Synthesis of PFS-b-poly(γ-benzyl-L-glutamate); Bz = benzyl.

methanol yielded a three-component polymeric mixture.[115] The mixture comprised of the amino-telechelic organometallic block and its nonfunctionalized counterpart, along with a significant amount of the corresponding dimer. Since the protective group is labile toward methanol, complete deprotection was accomplished upon precipitation. The amino-telechelic chains, isolated by silica gel column chromatography, served as macroinitiators for the ROP of the α-amino acid-*N*-carboxyanhydride. The resulting copolymers exhibited thermotropic liquid-crystalline behavior in bulk and thermoreversible gelation by a nanoribbon mechanism occurring in toluene.[116] Hydrogenation of the polypeptide block with H_2/Pd resulted in amphiphilic PFS-*b*-poly(L-glutamic acid).

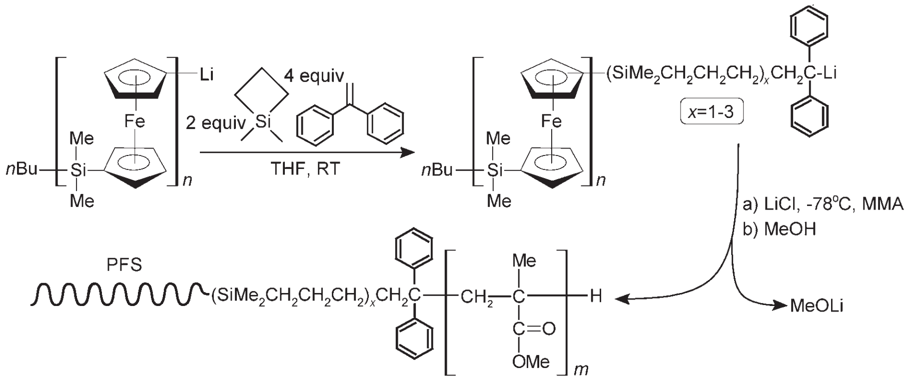
Graft copolymers were prepared by grafting living PFS onto poly[styrene-*co*-(4-chloromethylstyrene)] (Scheme 25).[117] Direct reaction of polysilaferrocenyllithium with the macromolecular multifunctional linking agent was unsuccessful. However, in the presence of a catalytic amount of CsI an insoluble product formed, presumably a result of cross-linking caused by lithium–halogen exchange and/or single-electron-transfer reactions and subsequent interchain nucleophilic substitution reactions. Suppression of these side reactions was achieved by end-capping the living arm with a 1,1-diphenylethylene (DPE) unit. The DPE end-capping reaction was found to be virtually quantitative by ^{1}H NMR spectroscopy. However, related exhaustive MALDI-TOF MS studies revealed incomplete conversion.[118]



Scheme 25. Synthesis of poly{[styrene-*co*-(4-chloromethylstyrene)]-g-ferrocenyldimethylsilane}.

Well-defined high-molecular-weight PFS-*b*-PMMA was synthesized through an exclusively living anionic process (Scheme 26).[119] The conventional sequential addition technique failed to produce the copolymer because of premature termination. Particularly, polysilaferrocenyllithium, even at −78 °C and in the presence of a 10-fold excess of LiCl, was found to react with the carbonyl group of MMA, resulting in quantitative formation of vinyl ketone functionalized chains. To overcome this problem, the living chain termini were treated with DPE to reduce their reactivity, prior to the MMA polymerization. Since the direct end-capping method suffered from incomplete conversion, DPE and 1,1-dimethylsilacyclobutane (DMSB) were added in succession to the reaction mixture to accelerate the modification of the chain termini. The thus generated sterically encumbered carbanion served as macroinitiator for the polymerization of MMA at −78 °C. Pentablock terpolymers PMMA-*b*-PFS-*b*-PS-*b*-PFS-*b*-PMMA were synthesized by using the same strategy and lithium naphthalide as a difunctional initiator.[120]

Linear dendritic diblock copolymers were synthesized by grafting living PFS onto the benzyl chloride group of first- or second-generation poly(benzyl ether) dendrons.[121] Polyferrocenylphenylphosphine (PFP) block copolymers (PFP-*b*-PDMS, PFP-*b*-PFS, PS-*b*-PFP, and PI-*b*-PFP) were also



Scheme 26. Synthesis of high-molecular-weight PFS-*b*-PMMA.

prepared by sequential living anionic polymerization.[122] The organometallic block contains coordinating atoms suitable for further functionalization. Reaction of PFP-*b*-PDMS with [Pd(1,5-cod)Cl_2] and [$Fe(CO)_4$(thf)] resulted in partial metal coordination with $PdCl_2$ and {$Fe(CO)_4$}, respectively.[123]

3.2. Chemical Modification

Pre- and postpolymerization approaches were both successfully applied for the synthesis of chemically modified PFS-based materials.[124] Generally, owing to the inherent sensitivity of PFS towards chain cleavage, strong reaction conditions should be avoided. PFS-bearing olefinic groups were quantitatively functionalized by hydrosilylation, whereas attempts to hydrosilylate the monomer failed.[125] Hydrosilylation was also applied for the synthesis of calamitic thermotropic side-chain liquid-crystalline polymers.[126]

Tetrapeptide segments Gly-Ala-Gly-Ala were grafted onto ω-amino-terminated PFS and PFS-bearing pendant amino groups, producing telechelic and side-chain-functionalized PFS, respectively.[127] The ability of this tetrapeptide sequence to form antiparallel β sheets is retained in the metallopolymer–peptide conjugates and phase separation occurs.

The first hydrophilic and water-soluble high-molecular-weight PFS was reported in 2000.[128] The applied methods were ROP of the Si(OR)$_2$-bridged monomers (R = CH_2CH_2OMe, $CH_2CH_2OCH_2CH_2OMe$) in the presence of Karstedt's catalyst and treatment of polyferrocenylchloromethylsilane with $Me_2NCH_2CH_2OH$ or oligo(ethylene glycol) monomethyl ether. Quaternization of the dimethylamino groups yielded the related cationic polyelectrolytes. Later on, various anionic and cationic polyelectrolytes were developed.[129] It has been demonstrated that a cationic PFS is an efficient DNA condensation and transfection agent.[129h] Redox-controlled permeability and swellability of composite-wall microcapsules has been achieved by using PFS polyelectrolytes.[129i] PFS-based water-soluble cationic and anionic polyelectrolytes were shown to self-assemble in a layer-by-layer fashion on primed Au, Si, and quartz substrates to create electrostatic superlattices.[130]

4. Self-Assembly

4.1. PFS Block Copolymers in the Solid State

The solubility parameter—the simplest numerical value indicating the solubility behavior of a polymer, which is derived from the cohesive energy density and thus from the (for polymers hypothetical) heat of vaporization—of the linear polyferrocenyldimethylsilane (PFMS) was determined by swelling measurements to be $\delta = 18.7(7)\ \mathrm{MPa}^{1/2}$.[131] This value renders PFMS immiscible with many polymers. Therefore, a wide variety of microphase-separated morphologies are expected for the related block copolymers.[132] No staining is required for the TEM experiments because of the larger scattering power of the iron-containing organometallic domains compared to the domains of the common organic polymers, providing sufficient contrast for TEM micrographs. For example, in bright-field TEM images PFS areas are dark whereas the PS areas are lighter. TEM, small-angle X-ray scattering (SAXS), and rheology experiments on neat PS-*b*-PFMS and its blends with the parent homopolymers allowed plotting of the phase diagram (Figure 2).[133]

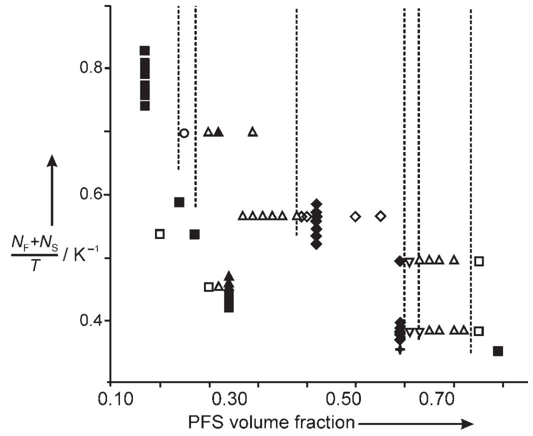


Figure 2. Phase diagram of PS-*b*-PFMS diblock/homopolymer blends; *y* axis: $N_S + N_F$ = overall degree of polymerization of the copolymer (F = ferrocenyldimethylsilane, S = styrene); *x* axis: overall PFS volume fraction; -----: phase boundaries between different ordered morphologies (symbols: ◆ lamellae, ▲ hexagonally packed cylinders, ▼ double gyroid, ● body-centered cubic-packed spheres, ■ disordered, + perforated lamellae). Neat diblocks and blends are displayed as solid and open symbols, respectively.

The microphase behavior of PMMA-*b*-PFMS with different compositions ($\phi_{PFS} = 0.25$–0.48; ϕ = volume fraction) was investigated by TEM (Figure 3).[134] Since no gyroidic morphologies were observed, the overall behavior of PMMA-*b*-PFMS indicates that PFMS is highly immiscible with PMMA, representing a system in the strong segregation regime.

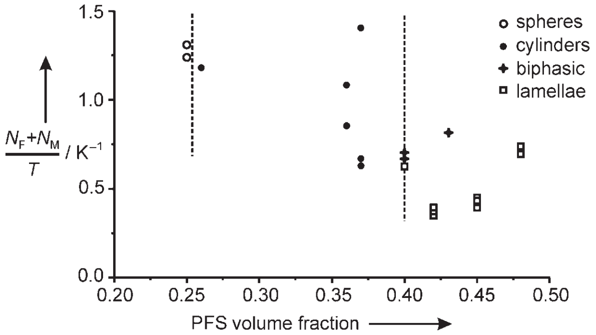


Figure 3. PMMA-*b*-PFMS phase diagram; *y* axis: N_F+N_M = overall degree of polymerization of the copolymer (F = ferrocenyldimethylsilane, M = methyl methacrylate); -----: phase boundaries between spherical and cylindrical morphology ($\phi_F \approx 0.25$), and between cylindrical and lamellar morphology ($\phi_F \approx 0.40$).

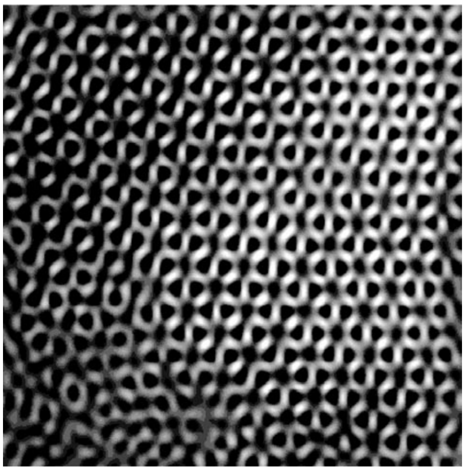


Figure 4. TEM image of a blend (overall $\phi_{PFMS}=0.39$) comprised of a PMMA-*b*-PFMS copolymer ($\phi_{PFMS}=0.45$, $M_n=27.1$ kDa) and 6 vol.% PMMA homopolymer ($M_n=9.6$ kDa). Annealing at 190 °C resulted in a gyroidic morphology. Reprinted with permission from Ref. [135]. Copyright 2004 American Chemical Society.

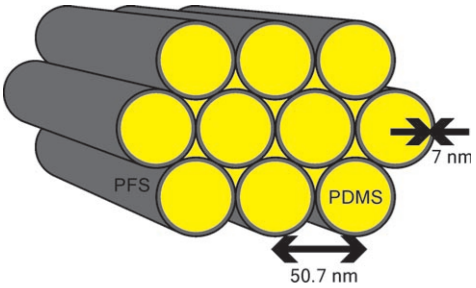


Figure 5. Schematic representation of the bulk morphology of a highly asymmetric PFMS-*b*-PDMS.

However, a bicontinuous gyroidic morphology was observed by blending lower-molecular-weight PMMA-*b*-PFMS with a relatively low amount (6 vol.%) of a PMMA homopolymer (Figure 4).[135]

The bulk microphase segregation of an asymmetric PFMS-*b*-PDMS copolymer ($\phi_{PDMS}=0.20$) was examined by SAXS, bright-field-mode TEM, high-resolution dark-mode scanning TEM, and electron-energy-loss spectroscopy.[136] The presence of iron in the PFS block complicates interpretation of the SAXS data as iron fluoresces upon absorption of the $Cu_{K\alpha}$ radiation. By using $Co_{K\alpha}$ radiation, the iron fluorescence can be avoided. The results support an unusual morphology of concentric cylinders in a PDMS matrix (Figure 5).

The behavior of an amorphous PS-*b*-polyferrocenylethylmethylsilane copolymer ($\phi_{PS}=0.48$) under periodic, strong 3D confinement was studied by TEM and energy-dispersive X-ray spectroscopy (EDX).[137] The copolymer, which affords well-defined lamellae in the bulk state, was self-assembled inside two different templates. In one case, ordered, interconnected copolymer spheres surrounded by air voids were produced. The strong curvature of this template results in the lamellae wrapping together to form concentric shells. In the other case, the replica was a matrix of the copolymer surrounding ordered spherical voids. Because of the strong confinement imposed by the surrounding silica spheres, the lamellae are oriented perpendicularly to the sphere surfaces. The periodic and interconnected nature of the template forces the lamellae to curve, branch, and join, thereby forming a phase that follows the topology of the void space. Clearly, the effects of strong 3D confinement altered both the lamellar structure and its thickness in comparison with the equilibrium bulk state (Figure 6).

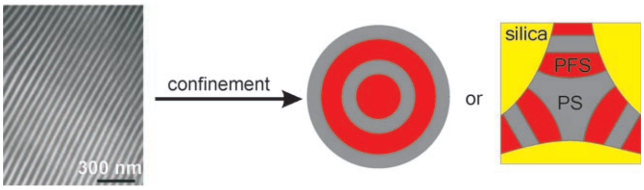


Figure 6. Morphology of an amorphous PS-*b*-polyferrocenylethylmethylsilane under periodic, strong three-dimensional confinement. Reprinted with permission from Ref. [137]. Copyright 2005 American Chemical Society.

Large area ordering at room temperature in thin films of PI-*b*-PFMS was achieved by introducing a low percentage of ferrocenylethylmethyl units in the organometallic block, thereby effectively suppressing the PFMS crystallization.[138]

4.2. PFS Block Copolymers in Selective Solvents

PFS-containing block copolymers self-assemble into micelles upon exposure to selective solvents.[139] In most cases the morphology is guided by the crystallization of the PFMS block.[140] Organometallic nanotubes were prepared from the self-assembly of highly asymmetric PFMS-*b*-PDMS in *n*-hexane and *n*-decane.[141] Time- and temperature-dependence studies revealed that a variety of morphologies are formed initially, depending on the conditions of sample preparation, but most of them eventually rearrange to form nanotubules. TEM analysis suggests that the resulting micelles are hollow. Encapsulation of *n*-butylferrocene and $Pb\textit{n}Bu_4$ confirmed the presence of a cavity within the tubes.

The PFMS blocks aggregate and crystallize to form a shell with a cavity in the middle of the tube, while the PDMS blocks form the corona. A model was proposed, comprising from a ribbonlike monolayer of extended PFS chains that fold back upon themselves, with the PDMS corona chains protruding from the edge of the ribbon (Figure 7). Finally, the nanotubes formed at room temperature in *n*-decane rearrange reversibly to generate short dense rods upon heating at 50 °C and aging.[142] This reversible transition reflects the dynamic nature of the self-assembled structures and demonstrates that both the tubes and the rods are equilibrium structures.

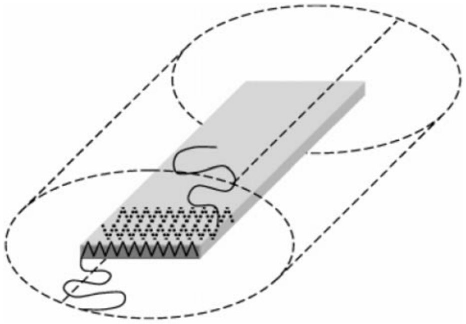


Figure 7. Proposed model for the PFMS-*b*-PDMS self-assembly in *n*-decane. The PFMS chains have a zigzag structure corresponding to their structure in the crystalline homopolymer, with a 6.4 Å spacing between Fe atoms on adjacent chains. The PFMS chains are drawn as extended in the direction perpendicular to the long axis of the ribbon. The dashed line surrounding the structure represents the space occupied by the PDMS corona. Reprinted with permission from Ref. [141d]. Copyright 2005 American Chemical Society.

Self-assembly and shell cross-linking of PFS-*b*-PMVS (PMVS = polymethylvinylsiloxane) leads to stable organometallic nanotubes with redox activity and tunable swellability.[143] These shell-cross-linked nanotubes were used for the redox-induced synthesis and encapsulation of metal nanoparticles.[144] Moreover, stable organometallic cylinders with tunable swellability were created by cross-linking the shell of cylindrical PI-*b*-PFS micelles.[145] The presence of a cross-linked corona was found to permit the pyrolysis-induced formation of cylindrical ceramic replicas containing size- and separation-tunable arrays of Fe nanoclusters. In addition, microfluidic channel-assisted alignment and patterning of the cross-linked cylinders were achieved.

5. Patternable PFSs

5.1. Micropatterning of Homopolymers and Random Copolymers

PFS is relatively resistant against reactive ion etching (RIE) compared to organic polymers. Large-area PFS patterns were fabricated by using various soft lithographic techniques, which afterwards transferred into the underlying substrate by RIE treatment. A protecting oxide layer acts as a mask, allowing access to structures with high aspect ratios.[146] Similarly, an ordered 2D array of ferromagnetic Fe/Co nanoparticle rings is formed from a PFS precursor that is highly metallized with cobalt clusters after plasma and pyrolytic treatment.[147] Magnetically tunable ceramic replicas are generated upon pyrolysis of freely standing cross-linked PFS films formed by micromolding techniques.[148]

Highly regular concentric ring patterns of PFS on Si substrate are formed by placing a drop of polymeric solution within a confined geometry and allowing the solvent to evaporate.[149] Subsequent pyrolytic treatment at 1000 °C generates magnetic ceramic rings containing α-Fe crystallites embedded within a SiC/C matrix.

PFSs bearing pendant methacrylate groups were used as negative-tone photoresists.[150] A PFS bearing metal carbonyl moieties was also used as a negative-tone photoresist and an electron-beam resist (Figure 8).[151] The main disadvantages of these lithographic approaches are the poor resolution and the development from organic solvents. The patterned features can afford magnetic ceramics either by pyrolysis or RIE in a secondary magnetic field.[152]

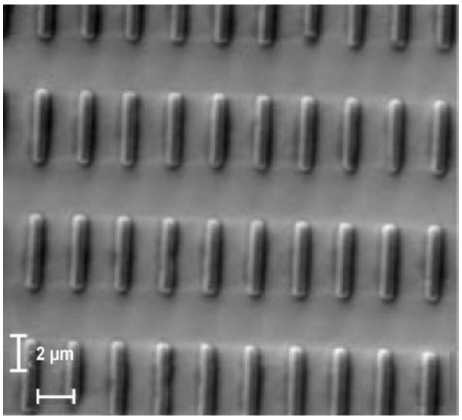


Figure 8. SEM image of PFS structures functionalized with cobalt clusters obtained by electron-beam lithography. Reprinted with permission from Ref. [151b].

Tunable microcellular morphologies are obtained upon exposure of PFS-based polymers to supercritical carbon dioxide.[153] Surface-constrained polymeric foams with submicron cell sizes can be generated by judicious selection of exposure conditions.

Pt^0-catalyzed copolymerization of [$fcSiMe_2$] and the spirocyclic cross-linker [$fcSi(CH_2)_3$] affords PFS microspheres under mild conditions.[154] Chemical oxidation of these microspheres leads to positively charged particles which undergo electrostatically driven self-assembly with negatively charged silica microspheres to form core–corona composite particles (Figure 9). Upon pyrolysis, the microspheres are transformed with shape retention into magnetically tunable ceramic replicas, which can be organized into ordered 2D arrays at the air–water interface under the influence of an external applied magnetic field.

The fabrication of multilayer films was achieved by layer-by-layer deposition of PFS-based polyelectrolytes.[155] Cation-

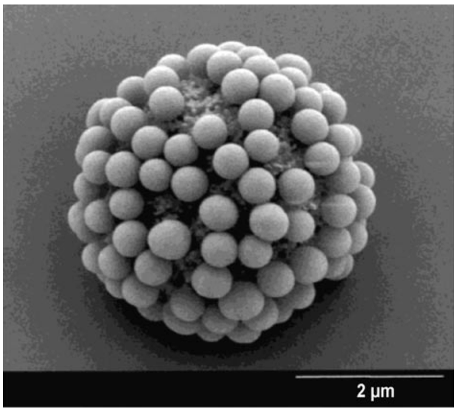


Figure 9. SEM micrograph of negatively charged silica microspheres electrostatically bound to the surface of positively charged PFS particles. Reprinted with permission from Ref. [154b]. Copyright 2002 American Chemical Society.

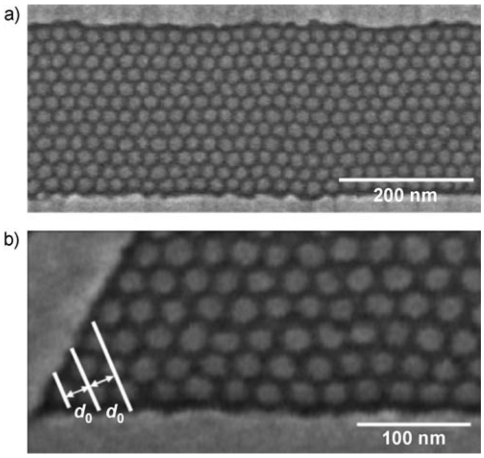


Figure 10. SEM images of PS-*b*-PFS domains in a) a 1D template in which an ordered array of PFS spheres is formed and b) in a 2D template, which allows the domain positions to be registered to a high accuracy by a sharp 60° corner. Reprinted with permission from Ref. [160a].

ic and anionic polyelectrolytes were deposited electrostatically onto a variety of substrates including quartz, silicon, gold, and hydrophilic/hydrophobic-patterned substrates.

5.2. PFS-Assisted Block Copolymer Nanopatterning

Various nanopatterning methodologies have been applied for PFS block copolymers. Self-assembled PI-*b*-PFS[156] and PS-*b*-PFS[157] thin films on silicon substrate were used for one-step lithography induced by RIE and pyrolysis, respectively. Remarkably, the former organometallic domains retain their original structure and no change in domain spacing occurs.

By exploiting the block copolymer lithography strategy it was possible to form large-area cobalt magnetic dot arrays of high density.[158] A PS-*b*-PFS copolymer self-assembles to form PFS spheres embedded in a PS matrix, thereby acting as a template for the successive etching steps on a multilayer substrate.

A graphoepitaxial—a technique whereby an artificial surface relief structure is used for the induction of crystallographic orientation in thin films—methodology was used for patterning a PS-*b*-PFS copolymer with $\phi_{\mathrm{PFS}} = 0.20$ and spherical equilibrium morphology in the bulk state.[159] The copolymer behaves elastically and can conform to various groove widths, leading to PFS sphere arrays with tunable row spacings that depend on the commensurability between the groove and the copolymer grain size. The well-ordered domain patterns were transferred into the underlying silica through a CHF_3-RIE process. Pattern registration is achievable under optimized templated self-assembly processing conditions (Figure 10).[160]

A modified soft-lithography protocol was applied, wherein submicron patterns of PS-*b*-PFS were generated on a silicon wafer by using an elastomeric mold against solutions of the copolymer.[161] After separation of the mold from the substrate, the sample was annealed and subsequently treated in oxygen plasma, affording linearly aligned ceramic spheres.

Fabrication of oriented ceramic nanolines was achieved by a multistep methodology using cylindrical micelles of PFS-*b*-PDMS or PFS-*b*-PI that exhibit a PFS core.[162] The micelles are formed in hexane and subsequently are coated onto a grooved substrate, formed by electron-beam lithography on PMMA. The deposition of the micelles inside the grooves is based on capillary forces. PMMA lift-off and subsequent plasma treatment lead to the oriented ceramic nanolines.

PS-*b*-PFS cannot be spread at the air–water interface because both of the components are hydrophobic. However, a polymer blend composed of symmetric PS-*b*-PFS and PS-*b*-P2VP [P2VP = poly(2-vinylpyridine)] forms Langmuir–Blodgett films.[163]

PFS block copolymers were used as catalyst precursors for templated carbon nanotube (CN) grown.[164] Self-assembled PFS domains are converted into well-ordered iron nanoparticles with a narrow size distribution, thus enabling the generation of high-quality single-wall CNs (SWCNs).[165] More importantly, catalyst patterns can be readily generated by using conventional semiconductor processing. SWCNs were grown on lithographically predefined sites over a very large area (Figure 11). Field-effect transistors containing

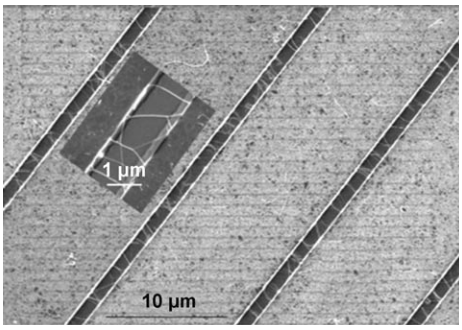


Figure 11. SEM image of SWCNs at predefined locations. Reprinted with permission from Ref. [165c]. Copyright 2006 American Chemical Society.

high-purity SWCN channels were fabricated with this protocol.[166]

6. Physical Properties and Potential Applications

Solution characterization of PFMS in THF revealed a more compact random-coil conformation relative to PS.[167]

PFSs can be fabricated into films, shapes, and fibers by using conventional polymer processing techniques.[168] ROP within various templates affords nanostructured materials.[169] Langmuir–Blodgett monolayers and films of polyferrocenylmethylstearylsilane have also been reported.[170]

PFMS, which is by far the most studied polyferrocenylsilane, is an amber thermoplastic, exhibiting a T_g value at 33 °C and melt transition temperature T_m in the range 122–145 °C. The T_g value follows the equation $T_g = T_{g,\infty} - K M_n^{-2/3}$ (T_g = glass transition temperature, $T_{g,\infty}$ = glass transition temperature at infinite chain length), reaching the maximum at a length of approximately 90 repeating units. The multiple T_m values arise from the presence of crystallites of different size, which melt at slightly different temperatures.[171] Whilst a similar melting behavior exists also for the symmetrically substituted analogues with short n-alkyl groups (C_2–C_5), the n-hexyl counterpart is amorphous. Thermal transition data for various silicon pendant groups are listed in Tables 10 and 11.[172] Crystallization kinetics of PFMS suggest a 3D spherulitic growth and an instantaneous nucleation mechanism.[173]

Table 10: Thermal transition data for [{(C_5H_4)$_2$FeSiR$_2$}$_n$] homopolymers.

R	T_g (T_m) [°C]
H	16 (165)
Me	33 (122–145)
Et	22 (91, 108)
*n*Pr	24 (98)
*n*Bu	3 (116, 129, 134)
*n*Pen	−11 (80–105)
*n*Hex	−26
OMe	19 (80–103)
OEt	0
OCH_2CF_3	16
O*n*Bu	−43
OHex	−51
$O(CH_2)_{11}CH_3$	(−30)
$O(CH_2)_{17}CH_3$	(32)
OC_6H_5	54
Cl	29 (156, 185)
$CH_2CH_2OCH_3$	−31
$(CH_2CH_2O)_2CH_3$	−53
OC_6H_4-*p*-*t*Bu	89
OC_6H_4-*p*-Ph	97

An insight to the possible conformations of PFMS chains in the solid state was obtained by single-crystal X-ray diffraction of well-defined oligomers and by molecular-mechanics calculations.[174] These studies suggest a parallel packing of *trans*-planar zigzag polymer chains (Figure 12). X-ray diffraction techniques on films and fibers revealed the coexistence of a 3D monoclinic crystalline polymer phase and a 2D mesophase with hexagonal or tetragonal packing of the chains.[175] Compared to polyvinylferrocene, which possesses a high T_g value, PFMS is much more conformationally flexible, probably owing to the ability of the iron atom in each ferrocene unit to act as a freely rotating "molecular ball bearing".

Table 11: Thermal transition data for [{(C_5H_4)$_2$FeSiMeR}$_n$] homopolymers.

R	T_g (T_m) [°C]
H	9 (87, 102)
Et	15
$CH_2CH_2CF_3$	59
$CH{=}CH_2$	28
n$C_{18}H_{37}$	1 (16)
Ph	90
ferrocenyl	99
5-norbornyl	81
Cl	59
$(CH_2)_3$NEtPh	26
$(CH_2)_3C_6H_4$-*p*-OMe	62
$(CH_2)_3$-*N*-carbazole	68
$(CH_2)_3$Cl	38
$(CH_2)_3$I	45
$(CH_2)_3$Br	41
CH_2Cl	25
$(CH_2)_2$Cl	14
$OCH_2CH{=}CH_2$	8
$CH_2CH{=}CH_2$	7
$CH_2CH_2SiEt_3$	−8

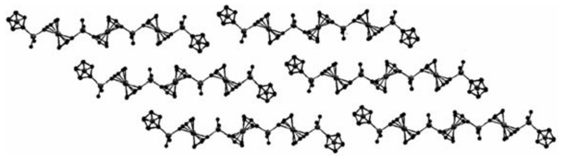


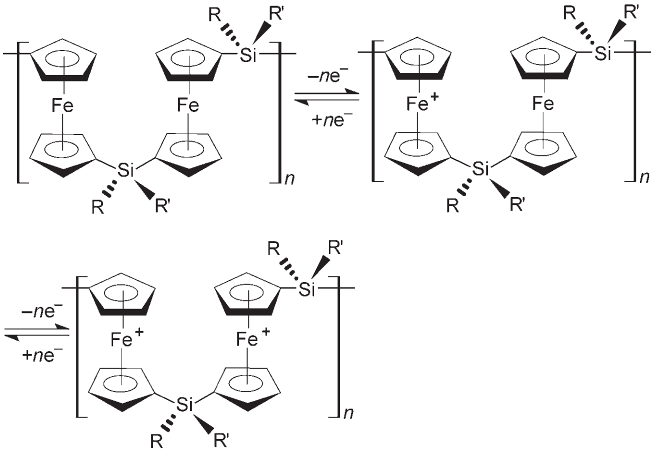
Figure 12. View of the crystal-packing arrangement of the pentamer analogue of PFMS parallel to the [011] plane showing three pairs of molecules. The terminal ferrocenyl groups are twisted in opposite directions perpendicularly to the interior, *trans*-planar, zigzag units. Periodicity along the macromolecular axis is 13.9 Å. Reprinted with permission from Ref. [86]. Copyright 1996 American Chemical Society.

The motions of PFS-based polymers were probed by using variable-temperature solid-state ^{2}H NMR spectroscopy.[176] The ferrocene moieties appear to be static on the NMR time scale in the case of the dimethyl and dimethoxy members, whereas high mobility above room temperature was observed in the case of the dihexyloxy counterpart. Solid-state ^{13}C NMR spectroscopy revealed that the main chains of the dimethyl and di-*n*-butyl analogues are fairly rigid in their crystalline lattices, although some libration (hindered tilt and rotational movements of the coupled ferrocenyl groups) is possible in the latter case, but the *n*-butyl side chains are very disordered.[177]

Single-molecule force microscopy studies revealed that the dimethyl and the methylphenyl members exhibit similar elasticity in their parent states, though they bear different side groups. However, upon oxidation the latter possesses larger enthalpic elasticity because of steric effects.[178] Moreover, an external chemical or electrochemical stimulus can be used to induce reversible elasticity changes of individual PFS chains on surfaces, which thus renders these materials suitable for redox-driven single-macromolecule-motor applications. The entropic elasticity of neutral PFMS chains (Kuhn length ca. 0.40 nm) was found to be larger compared to the oxidized ones (≈ 0.65 nm) in the region of lower force.[179]

Quasi-static mechanical analysis of PFMS revealed that it possesses approximately isotropic properties.[180] Studies of the optical properties of various polymetallocenes accessible by ROP revealed exceptionally high refractive indices with relatively low optical dispersion.[181] PFS-based polymers represent a suitable material for coating tapered optical fibers and measurement of subsequent environmentally induced changes in refractive index.[182]

The presence of two reversible oxidation waves in the cyclic voltammograms indicates a stepwise oxidation of the electroactive centers. Initially oxidation occurs at alternating iron sites as a consequence of interactions between the iron centers. Thus, as one iron center is oxidized, the neighboring sites become more difficult to oxidize and therefore do so at higher potential, resulting in two oxidation waves (Scheme 27). In contrast, polyvinylferrocene exhibits a single oxidation wave.[183] Electrochemical studies have been performed for polymeric films deposited on glassy carbon electrodes[184] and anchored PFS monolayers on gold surfaces.[185]



Scheme 27. Stepwise Fe^{II}/Fe^{III} redox process of PFS.

Since oxidation of PFS is accompanied by a color change from amber-yellow to green-blue, such materials have reversible electrochromic behavior. The conductivity of PFS materials, which are insulating ($\sigma \approx 10^{-14}$ S cm^{-1}) themselves, can be controllably increased by several orders of magnitude, to values typical of semiconductors ($\sigma \approx 10^{-8}$–10^{-4} S cm^{-1}), by oxidative doping.[186] However, the chemical oxidation process results in PFS chain cleavage to a significant extent.[187] The semiconductive nature of these polymers renders them excellent candidates as protective charge-dissipation coatings.[188] Photooxidation of amorphous polyferrocenylmethyl–phenylsilane thin films in the presence of chloroform and UV light leads to a significant increase of conductivity, potentially applicable to all-solid-state photoconducting and photovoltaic devices.[189]

Controlled cross-linking of PFS yields redox-active solvent-swellable gels, potentially applicable as electrochemical actuators or switches. The swelling of these gels in organic solvents depends on the degree of oxidation at the iron sites, thereby allowing the development of planar colloidal photonic crystal devices, in which silica microspheres are periodically arrayed in a cross-linked PFS matrix.[190]

Photoluminescence studies of composite materials comprised of CdSe nanocrystals and a $[\{(\eta^5\text{-}C_5H_4)_2FeX\}_n]$ polymer (X = SiMePh, PPh, or P(Ph)=S) revealed that the latter causes quenching of the band-edge photoluminescence of the quantum dots, both in solution and in thin films.[191] Moreover, PFMS is an effective quencher for platinum octaethylporphine phosphorescence in toluene solution.[192] Finally, the optical properties of colloidal photonic crystals can be tuned by using polyelectrolyte multilayers.[193]

7. Summary and Outlook

It seems reasonable to think that, with all the aforementioned fascinating properties, PFS-based materials will find commercial applications and play a crucial role in future technology, especially as part of the ongoing revolution based on nanotechnology and nanostructures. It is hard to find another polymeric material with such a range of promising and extraordinary properties. However, PFS materials are still in their initial stages of development. At the moment, the multistep synthetic procedures needed to access PFS building blocks as well as the scarcity of commercially available monomers render any bulk application unrealistic, since the price is prohibitively high.

Further establishment of structure–property relationships in PFS copolymers will enable the design of even more complex PFS-based materials with predetermined properties, whereby the constructive synergy of different moieties is utilized. However, this target relies mainly on the development of powerful versatile synthetic methodologies that will allow access to well-defined PFS-based copolymers that bear the desirable functionalities. In particular, the inherent instability of the PFS backbone against chain cleavage should be focused on, and mild conditions should be applied for postpolymerization functionalization. So far, this issue has been addressed allusively, thus rendering the chemical modification difficult and opportunities for combining diverse chemistries and achieving hierarchical arrangement are thus limited. Construction of more sophisticated PFS structures represents a grand challenge and holds enormous potential for the understanding, tailoring, and optimization of the overall properties.

Received: October 27, 2006

---

[1] a) I. Manners, *Synthetic Metal-Containing Polymers*, VCH, Weinheim, **2004**; b) A. S. Abd-El-Aziz, *Macromol. Rapid Commun.* **2002**, *23*, 995.

[2] a) K. Kulbaba, I. Manners, *Macromol. Rapid Commun.* **2001**, *22*, 711; b) I. Korczagin, R. G. H. Lammertink, M. A. Hempenius, S. Golze, G. J. Vancso, *Adv. Polym. Sci.* **2006**, *200*, 91.
[3] D. E. Herbert, U. F. J. Mayer, I. Manners, *Angew. Chem.*, **2007**, *119*, 5152; *Angew. Chem. Int. Ed.*, **2007**, *46*, 5060.
[4] F. S. Arimoto, A. C. Haven, *J. Am. Chem. Soc.* **1955**, *77*, 6295.
[5] H. P. Withers, D. Seyferth, J. D. Fellmann, P. E. Garrou, S. Martin, *Organometallics* **1982**, *1*, 1283.
[6] P. F. Brandt, T. B. Rauchfuss, *J. Am. Chem. Soc.* **1992**, *114*, 1926.
[7] a) D. A. Foucher, B. Z. Tang, I. Manners, *J. Am. Chem. Soc.* **1992**, *114*, 6246; b) M. T. Nguyen, A. F. Diaz, V. V. Dement'ev, K. H. Pannell, *Chem. Mater.* **1993**, *5*, 1389.
[8] I. Manners, *Can. J. Chem.* **1998**, *76*, 371.
[9] a) H. Rosenberg, M. D. Rausch, US 3060215, **1962**; b) H. Rosenberg (US Air Force), US 3426053, **1969**.
[10] a) A. G. Osborne, R. H. Whiteley, R. E. Meads, *J. Organomet. Chem.* **1980**, *193*, 345; b) D. Seyferth, H. P. Withers, *Organometallics* **1982**, *1*, 1275.
[11] M. Rehahn, *Acta Polym.* **1998**, *49*, 201.
[12] a) H. W. Roesky, M. Lücke, *J. Chem. Soc. Chem. Commun.* **1989**, 748; b) H. W. Roesky, M. Lücke, *Angew. Chem.* **1989**, *101*, 480; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 493.
[13] S. Barlow, M. J. Drewitt, T. Dijkstra, J. C. Green, D. O'Hare, C. Whittingham, H. H. Wynn, D. P. Gates, I. Manners, J. M. Nelson, J. K. Pudelski, *Organometallics* **1998**, *17*, 2113.
[14] J. K. Pudelski, D. A. Foucher, C. H. Honeyman, A. J. Lough, I. Manners, S. Barlow, D. O'Hare, *Organometallics* **1995**, *14*, 2470.
[15] J. K. Pudelski, D. A. Foucher, C. H. Honeyman, P. M. Macdonald, I. Manners, D. O'Hare, *Macromolecules* **1996**, *29*, 1894.
[16] a) J. C. Green, *Chem. Soc. Rev.* **1998**, *27*, 263; b) P. J. Shapiro, *Coord. Chem. Rev.* **2002**, *231*, 67.
[17] a) P. Nguyen, G. Stojcevic, K. Kulbaba, M. J. MacLachlan, X.-H. Liu, A. J. Lough, I. Manners, *Macromolecules* **1998**, *31*, 5977; b) P. Nguyen, A. J. Lough, I. Manners, *Macromol. Rapid Commun.* **1997**, *18*, 953.
[18] W. Finckh, B.-Z. Tang, D. A. Foucher, D. B. Zamble, R. Ziembinski, A. Lough, I. Manners, *Organometallics* **1993**, *12*, 823.
[19] a) D. L. Zechel, K. C. Hultzsch, R. Rulkens, D.; Balaishis, Y. Ni, J. K. Pudelski, A. J. Lough, I. Manners, *Organometallics* **1996**, *15*, 1972; b) G. Calleja, F. Carre, G. Cerveau, P. Labbe, L. Coche-Guerente, *Organometallics* **2001**, *20*, 4211.
[20] M. J. MacLachlan, J. Zheng, K. Thieme, A. J. Lough, I. Manners, C. Mordas, R. LeSuer, W. E. Geiger, L. M. Liable-Sands, A. L. Rheingold, *Polyhedron* **2000**, *19*, 275.
[21] K. H. Pannell, V. V. Dementiev, H. Li, F. Cervantes-Lee, M. T. Nguyen, A. F. Diaz, *Organometallics* **1994**, *13*, 3644.
[22] J. K. Pudelski, R. Rulkens, D. A. Foucher, A. J. Lough, P. M. Macdonald, I. Manners, *Macromolecules* **1995**, *28*, 7301.
[23] H. Stoeckli-Evans, A. G. Osborne, R. H. Whiteley, *Helv. Chim. Acta* **1976**, *59*, 2402.
[24] W. Y. Chan, A. J. Lough, I. Manners, *Acta Crystallogr. Sect. E* **2005**, *61*, m375.
[25] A. Berenbaum, A. J. Lough, I. Manners, *Organometallics* **2002**, *21*, 4415.
[26] D. A. Foucher, A. J. Lough, I. Manners, J. Rasburn, J. G. Vancso, *Acta Crystallogr. Sect. C* **1995**, *51*, 580.
[27] M. J. MacLachlan, A. J. Lough, I. Manners, *Macromolecules* **1996**, *29*, 8562.
[28] F. Jäkle, E. Vejzovic, K. N. Power-Billard, M. J. MacLachlan, A. J. Lough, I. Manners, *Organometallics* **2000**, *19*, 2826.
[29] a) G. Calleja, F. Carre, G. Cerveau, R. J. P. Corriu, *C. R. Acad. Sci. Paris Ser. IIc* **1998**, *1*, 285; b) G. Calléja, G. Cerveau, R. J. P. Corriu, *J. Organomet. Chem.* **2001**, *621*, 46.
[30] Z. Wang, A. Lough, I. Manners, *Macromolecules* **2002**, *35*, 7669.
[31] a) J. M. Nelson, H. Rengel, I. Manners, *J. Am. Chem. Soc.* **1993**, *115*, 7035; b) J. M. Nelson, P. Nguyen, R. Petersen, H. Rengel, P. M. Macdonald, A. J. Lough, I. Manners, N. P. Raju, J. E. Greedan, S. Barlow, D. O'Hare, *Chem. Eur. J.* **1997**, *3*, 573.
[32] R. Rulkens, D. P. Gates, D. Balaishis, J. K. Pudelski, D. F. McIntosh, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **1997**, *119*, 10976.
[33] A. Berenbaum, H. Braunschweig, R. Dirk, U. Englert, J. C. Green, F. Jäkle, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 5765.
[34] H. Braunschweig, R. Dirk, M. Müller, P. Nguyen, R. Resendes, D. P. Gates, I. Manners, *Angew. Chem.* **1997**, *109*, 2433; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2338.
[35] R. Resendes, J. M. Nelson, A. Fischer, F. Jäkle, A. Bartole, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2001**, *123*, 2116.
[36] G. Masson, P. Beyer, P. W. Cyr, A. J. Lough, I. Manners, *Macromolecules* **2006**, *39*, 3720.
[37] M. Castruita, F. Cervantes-Lee, J. S. Mahmoud, Y. Zhang, K. H. Pannell, *J. Organomet. Chem.* **2001**, *637*, 664.
[38] a) D. A. Foucher, M. Edwards, R. A. Burrow, A. J. Lough, I. Manners, *Organometallics* **1994**, *13*, 4959; b) D. A. Foucher, I. Manners, *Makromol. Chem. Rapid Commun.* **1993**, *14*, 63.
[39] H. Stoeckli-Evans, A. G. Osborne, R. H. Whiteley, *J. Organomet. Chem.* **1980**, *194*, 91.
[40] K. Mochida, N. Shibayama, M. Goto, *Chem. Lett.* **1998**, 339.
[41] H. K. Sharma, F. Cervantes-Lee, J. S. Mahmoud, K. H. Pannell, *Organometallics* **1999**, *18*, 399.
[42] R. Rulkens, A. J. Lough, I. Manners, *Angew. Chem.* **1996**, *108*, 1929; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1805.
[43] F. Jäkle, R. Rulkens, G. Zech, D. A. Foucher, A. J. Lough, I. Manners, *Chem. Eur. J.* **1998**, *4*, 2117.
[44] D. L. Zechel, D. A. Foucher, J. K. Pudelski, G. P. A. Yap, A. L. Rheingold, I. Manners, *J. Chem. Soc. Dalton Trans.* **1995**, 1893.
[45] C. Angelakos, D. B. Zamble, D. A. Foucher, A. J. Lough, I. Manners, *Inorg. Chem.* **1994**, *33*, 1709.
[46] P. Jutzi, R. Krallmann, G. Wolf, B. Neumann, H.-G. Stammler, *Chem. Ber.* **1991**, *124*, 2391.
[47] J. B. Sheridan, A. J. Lough, I. Manners, *Organometallics* **1996**, *15*, 2195.
[48] T. J. Peckham, D. A. Foucher, A. J. Lough, I. Manners, *Can. J. Chem.* **1995**, *73*, 2069.
[49] F. Martinez-Alías, S. Barlow, J. S. Tudor, D. O'Hare, R. T. Perry, J. M. Nelson, I. Manners, *J. Organomet. Chem.* **1997**, *528*, 47.
[50] J. Tudor, S. Barlow, B. R. Payne, D. O'Hare, P. Nguyen, C. E. B. Evans, I. Manners, *Organometallics* **1999**, *18*, 2281.
[51] S. Zürcher, V. Gramlich, A. Togni, *Inorg. Chim. Acta* **1999**, *291*, 355.
[52] A. Bartole-Scott, R. Resendes, F. Jäkle, A. J. Lough, I. Manners, *Organometallics* **2004**, *23*, 6116.
[53] A. Bartole-Scott, A. J. Lough, I. Manners, *Polyhedron* **2006**, *25*, 429.
[54] W. C. Chan, A. Berenbaum, S. B. Clendenning, A. J. Lough, I. Manners, *Organometallics* **2003**, *22*, 3796.
[55] A. Berenbaum, F. Jäkle, A. J. Lough, I. Manners, *Organometallics* **2001**, *20*, 834.
[56] W. Y. Chan, S. B. Clendenning, A. Berenbaum, A. J. Lough, S. Aouba, H. E. Ruda, I. Manners, *J. Am. Chem. Soc.* **2005**, *127*, 1765.
[57] T. J. Peckham, A. J. Lough, I. Manners, *Organometallics* **1999**, *18*, 1030.
[58] H. Brunner, J. Klankermayer, M. Zabel, *J. Organomet. Chem.* **2000**, *601*, 211.
[59] I. R. Butler, W. R. Cullen, F. W. B. Einstein, S. J. Rettig, A. J. Willis, *Organometallics* **1983**, *2*, 128.
[60] C. H. Honeyman, D. A. Foucher, F. Y. Dahmen, R. Rulkens, A. J. Lough, I. Manners, *Organometallics* **1995**, *14*, 5503.
[61] P. W. Cyr, A. J. Lough, I. Manners, *Acta Crystallogr. Sect. E* **2005**, *61*, 457.

[62] C. E. B. Evans, A. J. Lough, H. Grondey, I. Manners, *New J. Chem.* **2000**, *24*, 447.
[63] J. M. Nelson, A. J. Lough, I. Manners, *Organometallics* **1994**, *13*, 3703.
[64] J. M. Nelson, A. J. Lough, I. Manners, *Angew. Chem.* **1994**, *106*, 1019; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 989.
[65] U. Vogel, A. J. Lough, I. Manners, *Angew. Chem.* **2004**, *116*, 3383; *Angew. Chem. Int. Ed.* **2004**, *43*, 3321.
[66] T. J. Peckham, P. Nguyen, S. C. Bourke, Q. Wang, D. G. Harrison, P. Zoricak, C. Russell, L. M. Liable-Sands, A. L. Rheingold, A. J. Lough, I. Manners, *Organometallics* **2001**, *20*, 3035.
[67] W. P. Freeman, J. M. Dysard, T. D. Tilley, A. L. Rheingold, *Organometallics* **2002**, *21*, 1734.
[68] a) M. A. Buretea, T. D. Tilley, *Organometallics* **1997**, *16*, 1507; b) V. K. Aggarwal, D. Jones, M. L. Turner, H. Adams, *J. Organomet. Chem.* **1996**, *524*, 263.
[69] C. E. Stanton, T. R. Lee, R. H. Grubbs, N. S. Lewis, J. K. Pudelski, M. R. Callstrom, M. S. Erickson, M. L. McLaughlin, *Macromolecules* **1995**, *28*, 8713.
[70] a) R. W. Heo, F. B. Somoza, T. R. Lee, *J. Am. Chem. Soc.* **1998**, *120*, 1621; b) R. W. Heo, J.-S. Park, J. T. Goodson, G. C. Claudio, M. Takenaga, T. A. Albright, T. R. Lee, *Tetrahedron* **2004**, *60*, 7225.
[71] R. W. Heo, J.-S. Park, T. R. Lee, *Macromolecules* **2005**, *38*, 2564.
[72] C. Arisandy, A. R. Cowley, S. Barlow, *J. Organomet. Chem.* **2004**, *689*, 775.
[73] D. L. Compton, T. B. Rauchfuss, *Organometallics* **1994**, *13*, 4367.
[74] C. P. Galloway, T. B. Rauchfuss, *Angew. Chem.* **1993**, *105*, 1407; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1319.
[75] D. L. Compton, P. F. Brandt, T. B. Rauchfuss, D. F. Rosenbaum, C. F. Zukoski, *Chem. Mater.* **1995**, *7*, 2342.
[76] a) K. C. Hultzsch, J. M. Nelson, A. J. Lough, I. Manners, *Organometallics* **1995**, *14*, 5496; b) A. Berenbaum, I. Manners, *Dalton Trans.* **2004**, 2057.
[77] H. Braunschweig, M. Homberger, C. Hu, X. Zheng, E. Gullo, G. Clentsmith, M. Lutz, *Organometallics* **2004**, *23*, 1968.
[78] H. Braunschweig, T. Kupfer, K. Radacki, *Angew. Chem.* **2007**, *119*, 1655; *Angew. Chem. Int. Ed.* **2007**, *46*, 1630.
[79] C. Elschenbroich, F. Paganelli, M. Nowotny, B. Neumüller, O. Burghaus, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1599.
[80] M. Tamm, A. Kunst, T. Bannenberg, E. Herdtweck, P. Sirsch, C. J. Elsevier, J. M. Ernsting, *Angew. Chem.* **2004**, *116*, 5646; *Angew. Chem. Int. Ed.* **2004**, *43*, 5530.
[81] M. Tamm, A. Kunst, E. Herdtweck, *Chem. Commun.* **2005**, 1729.
[82] A. Bartole-Scott, H. Braunschweig, T. Kupfer, M. Lutz, I. Manners, T. Nguyen, K. Radacki, F. Seeler, *Chem. Eur. J.* **2006**, *12*, 1266.
[83] a) J. K. Pudelski, I. Manners, *J. Am. Chem. Soc.* **1995**, *117*, 7265; b) J. K. Pudelski, D. A. Foucher, C. H. Honeyman, P. M. Macdonald, I. Manners, D. O'Hare, *Macromolecules* **1996**, *29*, 1894.
[84] F. Jäkle, R. Rulkens, G. Zech, J. A. Massey, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 4231.
[85] R. Rulkens, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **1994**, *116*, 797.
[86] R. Rulkens, A. J. Lough, I. Manners, S. R. Lovelace, C. Grant, W. E. Geiger, *J. Am. Chem. Soc.* **1996**, *118*, 12683.
[87] a) Y. Ni, R. Rulkens, J. K. Pudelski, I. Manners, *Macromol. Rapid Commun.* **1995**, *16*, 637; b) N. P. Reddy, H. Yamashita, M. Tanaka, *J. Chem. Soc. Chem. Commun.* **1995**, 2263.
[88] P. Gómez-Elipe, P. M. Macdonald, I. Manners, *Angew. Chem.* **1997**, *109*, 780; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 762.
[89] J. B. Sheridan, K. Temple, A. J. Lough, I. Manners, *J. Chem. Soc. Dalton Trans.* **1997**, 711.
[90] K. Temple, F. Jäkle, J. B. Sheridan, I. Manners, *J. Am. Chem. Soc.* **2001**, *123*, 1355.
[91] a) T. Mizuta, M. Onishi, K. Miyoshi, *Organometallics* **2000**, *19*, 5005; b) T. Mizuta, Y. Imamura, K. Miyoshi, H. Yorimitsu, K. Oshima, *Organometallics* **2005**, *24*, 990.
[92] T. Mizuta, Y. Imamura, K. Miyoshi, *J. Am. Chem. Soc.* **2003**, *125*, 2068.
[93] M. Tanabe, S. C. Bourke, D. E. Herbert, A. J. Lough, I. Manners, *Angew. Chem.* **2005**, *117*, 6036; *Angew. Chem. Int. Ed.* **2005**, *44*, 5886.
[94] M. Tanabe, I. Manners, *J. Am. Chem. Soc.* **2004**, *126*, 11434.
[95] M. Tanabe, G. W. M. Vandermeulen, W. Y. Chan, P. W. Cyr, L. Vanderark, D. A. Rider, I. Manners, *Nat. Mater.* **2006**, *5*, 467.
[96] R. Resendes, P. Nguyen, A. J. Lough, I. Manners, *Chem. Commun.* **1998**, 1001.
[97] T. Baumgartner, F. Jäkle, R. Rulkens, G. Zech, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2002**, *124*, 10062.
[98] Y. Hatanaka, S. Okada, T. Minami, M. Goto, K. Shimada, *Organometallics* **2005**, *24*, 1053.
[99] a) J. Rasburn, R. Petersen, T. Jahr, R. Rulkens, I. Manners, J. G. Vancso, *Chem. Mater.* **1995**, *7*, 871; b) J. Rasburn, D. A. Foucher, W. F. Reynolds, I. Manners, J. G. Vancso, *Chem. Commun.* **1998**, 843.
[100] a) E. Fossum, K. Matyjaszewsky, R Rulkens, I. Manners, *Macromolecules* **1995**, *28*, 401; b) R. Rulkens, R. Resendes, A. Varma, I. Manners, K. Muti, E. Fossum, P. Miller, K. Matyjaszewski, *Macromolecules* **1997**, *30*, 8165.
[101] R. N. Kapoor, G. Crawford, J. Mahmoud, V. V. Dementiev, M. T. Nguyen, A. F. Diaz, K. H. Pannell, *Organometallics* **1995**, *14*, 4944.
[102] T. J. Peckham, J. A. Massey, M. Edwards, I. Manners, D. A. Foucher, *Macromolecules* **1996**, *29*, 2396.
[103] J. B. Sheridan, P. Gomez-Elipe, I. Manners, *Macromol. Rapid Commun.* **1996**, *17*, 319.
[104] K. Temple, S. Dziadek, I. Manners, *Organometallics* **2002**, *21*, 4377.
[105] P. Gómez-Elipe, R. Resendes, P. M. Macdonald, I. Manners, *J. Am. Chem. Soc.* **1998**, *120*, 8348.
[106] A. Bartole-Scott, R. Resendes, I. Manners, *Macromol. Chem. Phys.* **2003**, *204*, 1259.
[107] K. Temple, A. J. Lough, J. B. Sheridan, I. Manners, *J. Chem. Soc. Dalton Trans.* **1998**, 2799.
[108] R. Rulkens, Y. Ni, I. Manners, *J. Am. Chem. Soc.* **1994**, *116*, 12121.
[109] Y. Ni, R. Rulkens, I. Manners, *J. Am. Chem. Soc.* **1996**, *118*, 4102.
[110] R. Resendes, J. Massey, H. Dorn, M. A. Winnik, I. Manners, *Macromolecules* **2000**, *33*, 8.
[111] J.-F. Gohy, B. G. G. Lohmeijer, A. Alexeev, X.-S. Wang, I. Manners, M. A. Winnik, U. S. Schubert, *Chem. Eur. J.* **2004**, *10*, 4315.
[112] a) X. Wang, M. A. Winnik, I. Manners, *Macromolecules* **2005**, *38*, 1928; b) X. S. Wang, M. A. Winnik, I. Manners, *Macromol. Rapid Commun.* **2002**, *23*, 210.
[113] I. Korczagin, M. A. Hempenius, G. J. Vancso, *Macromolecules* **2004**, *37*, 1686.
[114] X. S. Wang, M. A. Winnik, I. Manners, *Macromol. Rapid Commun.* **2003**, *24*, 403.
[115] K. T. Kim, G. W. M. Vandermeulen, M. A. Winnik, I. Manners, *Macromolecules* **2005**, *38*, 4958.
[116] K. T. Kim, C. Park, G. W. M. Vandermeulen, D. A. Rider, C. Kim, M. A. Winnik, I. Manners, *Angew. Chem.* **2005**, *117*, 8178; *Angew. Chem. Int. Ed.* **2005**, *44*, 7964.
[117] K. N. Power-Billard, P. Wieland, M. Schafer, O. Nuyken, I. Manners, *Macromolecules* **2004**, *37*, 2090.
[118] C. Kloninger, PhD thesis, TU Darmstadt, **2004**.
[119] C. Kloninger, M. Rehahn, *Macromolecules* **2004**, *37*, 1720.

[120] U. Datta, M. Rehahn, *Macromol. Rapid Commun.* **2004**, *25*, 1615.

[121] a) T. Chen, L. Wang, G. Jiang, J. Wang, X. Wang, J. Zhou, W. Wang, *Eur. Polym. J.* **2006**, *42*, 687; b) T. Chen, L. Wang, G. Jiang, J. Wang, X. Wang, J. Zhou, J. Wang, C. Chen, W. Wang, H. Gao, *J. Electroanal. Chem.* **2006**, *586*, 122.

[122] a) C. H. Honeyman, T. J. Peckham, J. A. Massey, I. Manners, *Chem. Commun.* **1996**, 2589; b) L. Cao, M. Winnik, I. Manners, *J. Inorg. Organomet. Polym.* **1998**, *8*, 215.

[123] T. J. Peckham, J. A. Massey, C. H. Honeyman, I. Manners, *Macromolecules* **1999**, *32*, 2830.

[124] a) Y.-Y. Liu, X. Zhang, H.-D. Tang, T.-J. Wang, J.-G. Qin, D.-Y. Liu, S.-J. Li, C. Ye, *Chin. J. Chem.* **2002**, *20*, 1199; b) K. T. Kim, J. Han, C. Y. Ryu, F. C. Sun, S. S. Sheiko, M. A. Winnik, I. Manners, *Macromolecules* **2006**, *39*, 7922; c) D. Zhao, B. Ren, S. Liu, X. Liu, Z. Tong, *Chem. Commun.* **2006**, 779.

[125] S. Hilf, P. W. Cyr, D. A. Rider, I. Manners, T. Ishida, Y. Chujo, *Macromol. Rapid Commun.* **2005**, *26*, 950.

[126] a) X.-L. Liu, D. W. Bruce, I. Manners, *J. Organomet. Chem.* **1997**, *548*, 49; b) X.-L. Liu, D. W. Bruce, I. Manners, *Chem. Commun.* **1997**, 289.

[127] G. W. M. Vandermeulen, K. T. Kim, Z. Wang, I. Manners, *Biomacromolecules* **2006**, *7*, 1005.

[128] K. N. Power-Billard, I. Manners, *Macromolecules* **2000**, *33*, 26.

[129] a) K. N. Power-Billard, T. J. Peckham, A. Butt, F. Jäkle, I. Manners, *J. Inorg. Organomet. Polym.* **2000**, *10*, 159; b) M. A. Hempenius, N. S. Robins, R. G. H. Lammertink, G. J. Vancso, *Macromol. Rapid Commun.* **2001**, *22*, 30; c) K. N. Power-Billard, I. Manners, *Macromol. Rapid Commun.* **2002**, *23*, 607; d) F. Jäkle, Z. Wang, I. Manners, *Macromol. Rapid Commun.* **2000**, *21*, 1291; e) M. A. Hempenius, G. J. Vancso, *Macromolecules* **2002**, *35*, 2445; f) M. A. Hempenius, F. F. Brito, G. J. Vancso, *Macromolecules* **2003**, *36*, 6683; g) Z. Wang, A. Lough, I. Manners, *Macromolecules* **2002**, *35*, 7669; h) Z. Y. Zhong, C. Lin, Y. Ma, M. A. Hempenius, M. C. Lok, M. M. Fretz, J. F. J. Engbersen, G. J. Vancso, W. E. Hennink, J. Feijen, *J. Controlled Release* **2006**, *116*, e81; i) Y. Ma, W. Dong, M. A. Hempenius, H. Möhwald, G. J. Vancso, *Nat. Mater.* **2006**, *5*, 724.

[130] a) M. Ginzburg, J. Galloro, F. Jäkle, K. N. Power-Billard, S. Yang, I. Sokolov, C. N. C. Lam, A. W. Neumann, I. Manners, G. A. Ozin, *Langmuir* **2000**, *16*, 9609; b) J. Halfyard, J. Galloro, M. Ginzburg, Z. Wang, N. Coombs, I. Manners, G. A. Ozin, *Chem. Commun.* **2002**, 1746.

[131] K. Kulbaba, M. J. MacLachlan, C. E. B. Evans, I. Manners, *Macromol. Chem. Phys.* **2001**, *202*, 1768.

[132] a) K. Temple, J. A. Massey, Z. Chen, N. Vaidya, A. Berenbaum, M. D. Foster, I. Manners, *J. Inorg. Organomet. Polym.* **1999**, *9*, 189; b) W. Li, N. Sheller, M. D. Foster, D. Balaishis, I. Manners, B. Annís, J.-S. Lin, *Polymer* **2000**, *41*, 719; c) R. G. H. Lammertink, D. J. Versteeg, M. A. Hempenius, G. J. Vancso, *J. Polym. Sci. Part A* **1998**, *36*, 2147; d) H. B. Eitouni, N. P. Balsara, H. Hahn, J. A. Pople, M. A. Hempenius, *Macromolecules* **2002**, *35*, 7765; e) H. B. Eitouni, N. P. Balsara, *J. Am. Chem. Soc.* **2004**, *126*, 7446; f) R. G. H. Lammertink, M. A. Hempenius, G. J. Vancso, *Langmuir* **2000**, *16*, 6245; g) R. G. H. Lammertink, M. A. Hempenius, G. J. Vancso, K. Shin, M. H. Rafailovich, J. Sokolov, *Macromolecules* **2001**, *34*, 942; h) D. A. Rider, K. N. Power-Billard, K. A. Cavicchi, T. P. Russell, I. Manners, *Macromolecules* **2005**, *38*, 6931; i) U. Datta, PhD thesis, TU Darmstadt, **2005**.

[133] R. G. H. Lammertink, M. A. Hempenius, E. L. Thomas, G. J. Vancso, *J. Polym. Sci. Part B* **1999**, *37*, 1009.

[134] C. Kloninger, D. Knecht, M. Rehahn, *Polymer* **2004**, *45*, 8323.

[135] C. Kloninger, M. Rehahn, *Macromolecules* **2004**, *37*, 8319.

[136] J. Raez, Y. Zhang, L. Cao, S. Petrov, K. Erlacher, U. Wiesner, I. Manners, M. A. Winnik, *J. Am. Chem. Soc.* **2003**, *125*, 6010.

[137] A. C. Arsenault, D. A. Rider, N. Tetreault, J. I.-L. Chen, N. Coombs, G. A. Ozin, I. Manners, *J. Am. Chem. Soc.* **2005**, *127*, 9954.

[138] M. Roerdink, M. A. Hempenius, G. J. Vancso, *Chem. Mater.* **2005**, *17*, 1275.

[139] a) T. Chen, L. Wang, G. Jiang, J. Wang, J. Wang, J. Zhou, *Polymer* **2005**, *46*, 5773; b) T. Chen, L. Wang, G. Jiang, J. Wang, X. J. Wang, J. Zhou, W. Wang, H. Gao, *Polymer* **2005**, *46*, 7585; c) L. Cao, I. Manners, M. A. Winnik, *Macromolecules* **2002**, *35*, 8258; d) K. N. Power-Billard, R. J. Spontak, I. Manners, *Angew. Chem.* **2004**, *116*, 1280; *Angew. Chem. Int. Ed.* **2004**, *43*, 1260; e) D. J. Frankowski, J. Raez, I. Manners, M. A. Winnik, S. A. Khan, R. J. Spontak, *Langmuir* **2004**, *20*, 9304; f) I. Korczagin, M. A. Hempenius, R. G. Fokkink, M. A. C. Stuart, M. Al-Hussein, P. H. H. Bomans, P. M. Frederik, G. J. Vancso, *Macromolecules* **2006**, *39*, 2306; g) L. Cao, J. A. Massey, T. J. Peckham, M. A. Winnik, I. Manners, *Macromol. Chem. Phys.* **2001**, *202*, 2947.

[140] a) J. Massey, K. N. Power, I. Manners, M. A. Winnik, *J. Am. Chem. Soc.* **1998**, *120*, 9533; b) J. A. Massey, K. Temple, L. Cao, Y. Rharbi, J. Raez, M. A. Winnik, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 11577; c) R. Resendes, J. Massey, H. Dorn, K. N. Power, M. A. Winnik, I. Manners, *Angew. Chem.* **1999**, *111*, 2738; *Angew. Chem. Int. Ed.* **1999**, *38*, 2570; d) R. Resendes, J. A. Massey, K. Temple, L. Cao, K. N. Power-Billard, M. A. Winnik, I. Manners, *Chem. Eur. J.* **2001**, *7*, 2414; e) X. S. Wang, M. A. Winnik, I. Manners, *Macromolecules* **2002**, *35*, 9146.

[141] a) J. Raez, R. Barjovanu, J. A. Massey, M. A. Winnik, I. Manners, *Angew. Chem.* **2000**, *112*, 4020; *Angew. Chem. Int. Ed.* **2000**, *39*, 3862; b) J. Raez, I. Manners, M. A. Winnik, *Langmuir* **2002**, *18*, 7229; c) J. Raez, I. Manners, M. A. Winnik, *J. Am. Chem. Soc.* **2002**, *124*, 10381; d) G. Guérin, J. Raez, I. Manners, M. A. Winnik, *Macromolecules* **2005**, *38*, 7819.

[142] J. Raez, J. P. Tomba, I. Manners, M. A. Winnik, *J. Am. Chem. Soc.* **2003**, *125*, 9546.

[143] X. Wang, M. A. Winnik, I. Manners, *Angew. Chem.* **2004**, *116*, 3789; *Angew. Chem. Int. Ed.* **2004**, *43*, 3703.

[144] X.-S. Wang, H. Wang, N. Coombs, M. A. Winnik, I. Manners, *J. Am. Chem. Soc.* **2005**, *127*, 8924.

[145] X. S. Wang, A. Arsenault, G. A. Ozin, M. A. Winnik, I. Manners, *J. Am. Chem. Soc.* **2003**, *125*, 12686.

[146] a) R. G. H. Lammertink, M. A. Hempenius, V. Z.-H. Chan, E. L. Thomas, G. J. Vancso, *Chem. Mater.* **2001**, *13*, 429; b) I. Korczagin, S. Golze, M. A. Hempenius, G. J. Vancso, *Chem. Mater.* **2003**, *15*, 3663.

[147] S. B. Clendenning, S. Fournier-Bidoz, A. Pietrangelo, G. Yang, S. Han, P. M. Brodersen, C. M. Yip, Z.-H. Lu, G. A. Ozin, I. Manners, *J. Mater. Chem.* **2004**, *14*, 1686.

[148] M. Ginzburg, M. J. MacLachlan, S. M. Yang, N. Coombs, T. W. Coyle, N. P. Raju, J. E. Greedan, R. H. Herber, G. A. Ozin, I. Manners, *J. Am. Chem. Soc.* **2002**, *124*, 2625.

[149] S. W. Hong, J. Xu, J. Xia, Z. Lin, F. Qiu, Y. Yang, *Chem. Mater.* **2005**, *17*, 6223.

[150] a) P. W. Cyr, D. A. Rider, K. Kulbaba, I. Manners, *Macromolecules* **2004**, *37*, 3959; b) J. Wang. L. Wang, X. Wang, T. Chen, H. Yu, W. Wang, C. Wang, *Mater. Lett.* **2006**, *60*, 1416.

[151] a) A. Y. Cheng, S. B. Clendenning, G. Yang, Z.-H. Lu, C. M. Yip, I. Manners, *Chem. Commun.* **2004**, 780; b) S. B. Clendenning, S. Aouba, M. S. Rayat, D. Grozea, J. B. Sorge, P. M. Brodersen, R. N. S. Sodhi, Z.-H. Lu, C. M. Yip, M. R. Freeman, H. E. Ruda, I. Manners, *Adv. Mater.* **2004**, *16*, 215.

[152] a) S. B. Clendenning, S. Han, N. Coombs, C. Paquet, M. S. Rayat, D. Grozea, P. M. Brodersen, R. N. S. Sodhi, C. M. Yip, Z.-H. Lu, I. Manners, *Adv. Mater.* **2004**, *16*, 291; b) B. Z. Tang, R. Petersen, D. A. Foucher, A. Lough, N. Coombs, R. Sodhi, I. Manners, *J. Chem. Soc. Chem. Commun.* **1993**, 523; c) R. Petersen, D. A. Foucher, B. Z. Tang, A. Lough, N. P. Raju, J. E.

Greedan, I. Manners, *Chem. Mater.* **1995**, *7*, 2045; d) A. Berenbaum, M. Ginzburg-Margau, N. Coombs, A. J. Lough, A. Safa-Sefat, J. E. Greedan, G. A. Ozin, I. Manners, *Adv. Mater.* **2003**, *15*, 51; e) K. Liu, S. B. Clendenning, L. Friebe, W. Y. Chan, X. Zhu, M. R. Freeman, G. C. Yang, C. M. Yip, D. Grozea, Z. Lu, I. Manners, *Chem. Mater.* **2006**, *18*, 2591.

[153] D. J. Frankowski, S. Fournier-Bidoz, I. Manners, G. A. Ozin, S. A. Khan, R. J. Spontak, *Macromol. Chem. Phys.* **2004**, *205*, 2398.

[154] a) K. Kulbaba, R. Resendes, A. Cheng, A. Bartole, A. Safa-Sefat, N. Coombs, H. D. H. Stöver, J. E. Greedan, G. A. Ozin, I. Manners, *Adv. Mater.* **2001**, *13*, 732; b) K. Kulbaba, A. Cheng, A. Bartole, S. Greenberg, R. Resendes, N. Coombs, A. Safa-Sefat, J. E. Greedan, H. D. H. Stöver, G. A. Ozin, I. Manners, *J. Am. Chem. Soc.* **2002**, *124*, 12522.

[155] M. A. Hempenius, N. S. Robins, M. Péter, E. S. Kooij, G. J. Vancso, *Langmuir* **2002**, *18*, 7629.

[156] R. G. H. Lammertink, M. A. Hempenius, J. E. Van den Enk, V. Z.-H. Chan, E. L. Thomas, G. J. Vancso, *Adv. Mater.* **2000**, *12*, 98.

[157] K. Temple, K. Kulbaba, K. N. Power-Billard, I. Manners, K. A. Leach, T. Xu, T. P. Russell, C. J. Hawker, *Adv. Mater.* **2003**, *15*, 297.

[158] a) J. Y. Cheng, C. A. Ross, E. L. Thomas, H. I. Smith, R. G. H. Lammertink, G. J. Vancso, *IEEE Trans. Magn.* **2002**, *38*, 2541; b) J. Y. Cheng, C. A. Ross, V. Z.-H. Chan, E. L. Thomas, R. G. H. Lammertink, G. J. Vancso, *Adv. Mater.* **2001**, *13*, 1174.

[159] a) J. Y. Cheng, C. A. Ross, E. L. Thomas, H. I. Smith, G. J. Vancso, *Appl. Phys. Lett.* **2002**, *81*, 3657; b) J. Y. Cheng, C. A. Ross, E. L. Thomas, H. I. Smith, G. J. Vancso, *Adv. Mater.* **2003**, *15*, 1599.

[160] a) J. Y. Cheng, F. Zhang, H. I. Smith, G. J. Vancso, C. A. Ross, *Adv. Mater.* **2006**, *18*, 597; b) J. Y. Cheng, A. M. Mayes, C. A. Ross, *Nat. Mater.* **2004**, *3*, 823.

[161] T. Deng, Y. Ha, J. Cheng, C. A. Ross, E. L. Thomas, *Langmuir* **2002**, *18*, 6719.

[162] a) J. A. Massey, M. A. Winnik, I. Manners, V. Z.-H. Chan, J. M. Ostermann, R. Enchelmaier, J. P. Spatz, M. Möller, *J. Am. Chem. Soc.* **2001**, *123*, 3147; b) L. Cao, J. A. Massey, M. A. Winnik, I. Manners, S. Riethmüller, F. Banhart, M. Möller, *Adv. Funct. Mater.* **2003**, *13*, 271.

[163] Y.-S. Seo, K. S. Kim, A. Galambos, R. G. H. Lammertink, G. J. Vancso, J. Sokolov, M. Rafailovich, *Nano Lett.* **2004**, *4*, 483.

[164] C. Hinderling, Y. Keles, T. Stockli, H. E. Kanpp, T. de los Arcos, P. Olehafen, T. Korczagin, M. A. Hempenius, G. J. Vancso, R. L. Pugin, H. Heinzelmann, *Adv. Mater.* **2004**, *16*, 876.

[165] a) S. Lastella, Y. J. Jung, H. C. Yang, R. Vajtai, P. M. Ajayan, C. Y. Ryu, D. A. Rider, I. Manners, *J. Mater. Chem.* **2004**, *14*, 1791; b) J. Q. Lu, T. E. Kopley, N. Moll, D. Roitman, D. Chamberlin, Q. Fu, J. Liu, T. P. Russell, D. A. Rider, I. Manners, M. A. Winnik, *Chem. Mater.* **2005**, *17*, 2227; c) J. Lu, T. Kopley, D. Dutton, J. Liu, C. Qian, H. Son, M. Dresselhaus, J. Kong, *J. Phys. Chem. B* **2006**, *110*, 10585; d) J. Q. Lu, D. A. Rider, E. Onyegam, H. Wang, M. A. Winnik, I. Manners, Q. Cheng, Q. Fu, J. Liu, *Langmuir* **2006**, *22*, 5174.

[166] S. Lastella, G. Mallick, R. Woo, S. P. Karna, D. A. Rider, I. Manners, Y. J. Jung, C. Y. Ryu, P. M. Ajayan, *J. Appl. Phys.* **2006**, *99*, 024302.

[167] J. A. Massey, K. Kulbaba, M. A. Winnik, I. Manners, *J. Polym. Sci. Part B* **2000**, *38*, 3032.

[168] a) M. J. MacLachlan, M. Ginzburg, N. Coombs, T. W. Coyle, N. P. Raju, J. E. Greedan, G. A. Ozin, I. Manners, *Science* **2000**, *287*, 1460; b) Z. Chen, M. D. Foster, W. Zhou, H. Fong, D. H. Reneker, R. Resendes, I. Manners, *Macromolecules* **2001**, *34*, 6156.

[169] a) M. Ginzburg-Margau, S. Fournier-Bidoz, N. Coombs, G. A. Ozin, I. Manners, *Chem. Commun.* **2002**, 3022; b) S. O'Brien, J. Tudor, S. Barlow, M. J. Drewitt, S. J. Heyes, D. O'Hare, *Chem. Commun.* **1997**, 641; c) S. O'Brien, J. M. Keates, S. Barlow, M. J. Drewitt, B. R. Payne, D. O'Hare, *Chem. Mater.* **1998**, *10*, 4088; d) J. Galloro, M. Ginzburg, H. Míguez, S. M. Yang, N. Coombs, A. Safa-Sefat, J. E. Greedan, I. Manners, G. A. Ozin, *Adv. Funct. Mater.* **2002**, *12*, 382; e) M. J. MacLachlan, M. Ginzburg, N. Coombs, N. P. Raju, J. E. Greedan, G. A. Ozin, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 3878; f) M. J. MacLachlan, P. Aroca, N. Coombs, I. Manners, G. A. Ozin, *Adv. Mater.* **1998**, *10*, 144; g) P. Ferreira, I. S. Gonçalves, F. Mosselmans, M. Pillinger, J. Rocha, A. Thursfield, *Eur. J. Inorg. Chem.* **2000**, 97; h) C. J. Miller, D. O'Hare, *J. Mater. Chem.* **2005**, *15*, 5070.

[170] H. Yim, M. D. Foster, D. Balaishis, I. Manners, *Langmuir* **1998**, *14*, 3921.

[171] R. G. H. Lammertink, M. A. Hempenius, I. Manners, G. J. Vancso, *Macromolecules* **1998**, *31*, 795.

[172] a) D. Foucher, R. Ziembinski, R. Petersen, J. Pudelski, M. Edwards, Y. Ni, J. Massey, C. R. Jaeger, G. J. Vancso, I. Manners, *Macromolecules* **1994**, *27*, 3992; b) H. Tang, Y. Liu, X. Chen, J. Qin, M. Inokuchi, M. Kinoshita, X. Jin, Z. Wang, B. Xu, *Macromolecules* **2004**, *37*, 9785; c) D. A. Foucher, R. Ziembinski, B. Z. Tang, P. M. Macdonald, J. Massey, C. R. Jaeger, G. J. Vancso, I. Manners, *Macromolecules* **1993**, *26*, 2878.

[173] R. G. H. Lammertink, M. A. Hempenius, G. J. Vancso, *Macromol. Chem. Phys.* **1998**, *199*, 2141.

[174] S. Barlow, A. L. Rohl, S. Shi, C. M. Freeman, D. O'Hare, *J. Am. Chem. Soc.* **1996**, *118*, 7578.

[175] V. S. Papkov, M. V. Gerasimov, I. I. Dubovik, S. Sharma, V. V. Dementiev, K. H. Pannell, *Macromolecules* **2000**, *33*, 7107.

[176] a) K. Kulbaba, P. M. Macdonald, I. Manners, *Macromolecules* **1999**, *32*, 1321; b) K. Kulbaba, I. Manners, P. M. Macdonald, *Macromolecules* **2002**, *35*, 10014.

[177] J. Rasburn, F. Seker, K. Kulbaba, P. G. Klein, I. Manners, G. J. Vancso, P. M. Macdonald, *Macromolecules* **2001**, *34*, 2884.

[178] W. Q. Shi, S. X. Cui, C. Wang, L. Y. Wang, X. Zhang, X. J. Wang, L. Wang, *Macromolecules* **2004**, *37*, 1839.

[179] a) S. Zou, M. A. Hempenius, H. Schönherr, G. J. Vancso, *Macromol. Rapid Commun.* **2006**, *27*, 103; b) S. Zou, I. Korczagin, M. A. Hempenius, H. Schönherr, G. J. Vancso, *Polymer* **2006**, *47*, 2483.

[180] C. W. Smith, K. H. Tan, K. E. Evans, R. Resendes, A. Bartole-Scott, I. Manners, *J. Polym. Sci. Part B* **2005**, *43*, 2280.

[181] a) C. Paquet, P. W. Cyr, E. Kumacheva, I. Manners, *Chem. Mater.* **2004**, *16*, 5205; b) C. Paquet, P. W. Cyr, E. Kumacheva, I. Manners, *Chem. Commun.* **2004**, 234.

[182] a) K. H. Pannell, J. Robillard (Univ Texas), US 5472786, **1995**; b) L. I. Espada, M. Shadaram, J. Robillard, K. H. Pannell, *J. Inorg. Organomet. Polym.* **2000**, *10*, 169.

[183] a) D. A. Foucher, C. H. Honeyman, J. M. Nelson, B. Z. Tang, I. Manners, *Angew. Chem.* **1993**, *105*, 1843; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1709; b) M. T. Nguyen, A. F. Diaz, V. V. Dement'ev, K. H. Pannell, *Chem. Mater.* **1994**, *6*, 952; c) X. J. Wang, L. Wang, J. J. Wang, *J. Polym. Sci. Part B* **2004**, *42*, 2245.

[184] a) X. J. Wang, L. Wang, J. J. Wang, T. Chen, *J. Phys. Chem. B* **2004**, *108*, 5627; b) T. Chen, L. Wang, G. Jiang, J. Wang, X. Dong, X. Wang, J. Zhou, C. Wang, W. Wang, *J. Phys. Chem. B* **2005**, *109*, 4624.

[185] a) M. Péter, R. G. H. Lammertink, M. A. Hempenius, M. van Os, M. W. J. Beulen, D. N. Reinhoudt, W. Knoll, G. J. Vancso, *Chem. Commun.* **1999**, 359; b) M. Péter, M. A. Hempenius, E. S. Kooij, T. A. Jenkins, S. J. Roser, W. Knoll, G. J. Vancso, *Langmuir* **2004**, *20*, 891; c) S. Zou, Y. J. Ma, M. A. Hempenius, H. Schönherr, G. J. Vancso, *Langmuir* **2004**, *20*, 6278; d) M. Péter, R. G. H. Lammertink, M. A. Hempenius, G. J. Vancso, *Langmuir* **2005**, *21*, 5115.

[186] a) L. Bakueva, E. H. Sargent, R. Resendes, A. Bartole, I. Manners, *J. Mater. Sci. Mater. Electron.* **2001**, *12*, 21; b) L. Espada, K. H. Pannell, V. Papkov, L. Leites, S. Bukalov, I. Suzdalev, M. Tanaka, T. Hayashi, *Organometallics* **2002**, *21*, 3758; c) K. H. Pannell, V. I. Imshennik, Yu. V. Maksimov, M. N. Il'ina, H. K. Sharma, V. S. Papkov, I. P. Suzdalev, *Chem. Mater.* **2005**, *17*, 1844; d) L. Wang, X. J. Wang, J. Pan, L. X. Feng, *J. Appl. Polym. Sci.* **2002**, *86*, 3508.

[187] M. I. Giannotti, H. Lv, Y. Ma, M. P. Steenvoorden, A. R. Overweg, M. Roerdink, M. A. Hempenius, G. J. Vancso, *J. Inorg. Organomet. Polym. Mater.* **2006**, *15*, 527.

[188] a) R. Resendes, A. Berenbaum, G. Stojevic, F. Jäkle, A. Bartole, F. Zamanian, G. Dubois, C. Hersom, K. Balmain, I. Manners, *Adv. Mater.* **2000**, *12*, 327; b) I. Manners, K. G. Balmain, C. H. Hersom (CT Res. Earth & Space Tech), US 6361869, **2002**; c) A. Bartole-Scott, A. Berenbaum, R. Resendes, I. Manners, G. Dubois, K. G. Balmain, *J. Inorg. Organomet. Polym. Mater.* **2006**, *15*, 485.

[189] a) P. W. Cyr, M. Tzolov, I. Manners, E. H. Sargent, *Macromol. Chem. Phys.* **2003**, *204*, 915; b) M. Tzolov, P. W. Cyr, E. H. Sargent, I. Manners, *J. Chem. Phys.* **2004**, *120*, 1990; c) P. W. Cyr, E. J. D. Klem, E. H. Sargent, I. Manners, *Chem. Mater.* **2005**, *17*, 5770.

[190] a) A. C. Arsenault, H. Miguez, V. Kitaev, G. A. Ozin, I. Manners, *Adv. Mater.* **2003**, *15*, 503; b) A. Arsenault, H. Miguez, G. A. Ozin, I. Manners, WO 2004034134, **2004**; c) A. C. Arsenault, V. Kitaev, I. Manners, G. A. Ozin, A. Mihi, H. Míguez, *J. Mater. Chem.* **2005**, *15*, 133.

[191] P. W. Cyr, M. Tzolov, M. A. Hines, I. Manners, E. H. Sargent, G. D. Scholes, *J. Mater. Chem.* **2003**, *13*, 2213.

[192] J. Yang, P. W. Cyr, Y. S. Wang, R. Soong, P. M. Macdonald, L. S. Chen, I. Manners, M. A. Winnik, *Photochem. Photobiol.* **2006**, *82*, 262.

[193] a) A. C. Arsenault, J. Halfyard, Z. Wang, V. Kitaev, G. A. Ozin, I. Manners, A. Mihi, H. Míguez, *Langmuir* **2005**, *21*, 499; b) F. Fleischhaker, A. C. Arsenault, Z. Wang, V. Kitaev, F. C. Peiris, G. von Freymann, I. Manners, R. Zentel, G. A. Ozin, *Adv. Mater.* **2005**, *17*, 2455.