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Organometallic Macrocycles and Cyclic Polymers by the Bipyridine-Initiated Photolytic Ring Opening of a Silicon-Bridged [1]Ferrocenophane**

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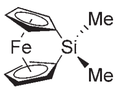
Cyclic organic polymers are challenging synthetic targets, and such materials show interesting and important differences in physical and chemical properties compared to their linear counterparts.[1] Although inorganic macrocyclic species have received significant attention, examples of cyclic inorganic polymers are quite scarce.[1,2] Organometallic macrocycles are even less common, and cyclic organometallic polymers are extremely rare.[3,4] Silicon-bridged [1]ferrocenophanes (sila[1]ferrocenophanes), such as **1**, possess substantial ring strain, and their ability to undergo ring-opening polymerization (ROP) to give linear oligo- and polyferrocenylsilanes (PFSs) has been well-studied.[5] In contrast, cyclic analogues of PFSs, the [1^n]ferrocenophanes,[6] are much less explored. The smallest of these cyclic species are the disila[1.1]ferrocenophanes **2**;[7] these species as well as many other [1.1]ferrocenophanes with bridging atoms other than silicon are well-known.[8] Nevertheless, analogues with larger ring sizes are more difficult to prepare, and only a few examples have been reported.[9,10] Accordingly, the preparation of high-molecular-weight cyclic organometallic polymers, such as cyclic PFS, remains a substantial synthetic challenge.[4]



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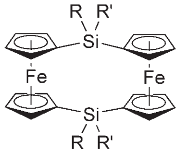

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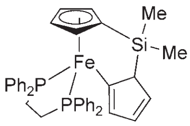

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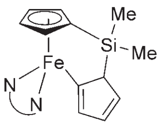
Recently, we developed photocontrolled ring-opening polymerizations of sila[1]ferrocenophanes (such as **1**) involving iron–cyclopentadienyl (Fe−Cp) bond cleavage; these reactions proceed in the presence of $[C_5H_5]^-$ anions and provide a controlled route to new PFS homopolymers and block copolymers.[11–13] When 1,2-bis(diphenylphosphino)ethane (dppe) was used in place of the $Na[C_5H_5]$ initiator at 5 °C, photolysis afforded ring-slipped species **3** as the sole product, and no polymer was detected.[11] To explore the generality of this unusual chemistry, we studied the analogous reaction in the presence of a bidentate N-donor ligand, 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy), as an initiator.[14]



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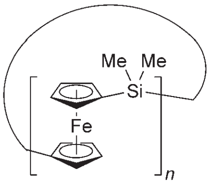

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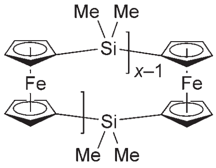

6_x

Photolysis of ferrocenophane **1** in the presence of a stoichiometric quantity of Me_2bpy was performed for 2 h at 35 °C in THF, and the initially red solution turned orange-brown. Surprisingly, analysis of the reaction mixture by ^1H NMR spectroscopy showed the complete conversion of ferrocenophane **1** into multiple products, including a polymer fraction (PFS **5**, 24 %) and cyclic dimer **6_2**.[2,15,16] The presence of cyclic dimer **6_2** and the moderate yield of PFS **5** prompted us to search for other cyclic oligomers in the reaction mixture:[17] pure cyclic dimer **6_2**, cyclic pentamer **6_5**, and cyclic hexamer **6_6** were obtained after extraction with hexanes and purification by flash chromatography. Cyclic oligomers **6_5** and **6_6** are rare examples of [1^n]ferrocenophanes containing more than two ferrocene units; they are also analogues of the linear oligoferrocenylsilanes that we have synthesized by the anionic oligomerization of ferrocenophane **1**.[18]

Cyclic pentamer **6_5** and cyclic hexamer **6_6** were fully characterized using NMR spectroscopy and X-ray crystallography.[16] As expected, the NMR spectra of these cyclic oligoferrocenylsilanes are much simpler than those of their linear analogues. For example, the ^1H NMR spectrum of cyclic pentamer **6_5** shows only two triplets for Cp protons at $\delta = 4.24$ and 4.04 ppm and a singlet for methyl protons at $\delta = 0.46$ ppm.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

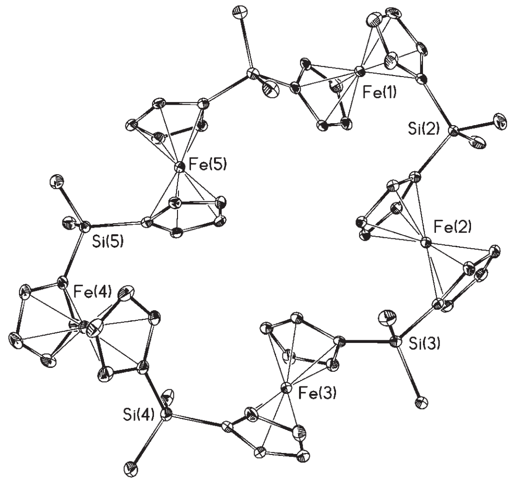


Figure 1. Molecular structure of $\mathbf{6}_5$. Thermal ellipsoids are set at the 30% probability level; hydrogen atoms have been removed for clarity.

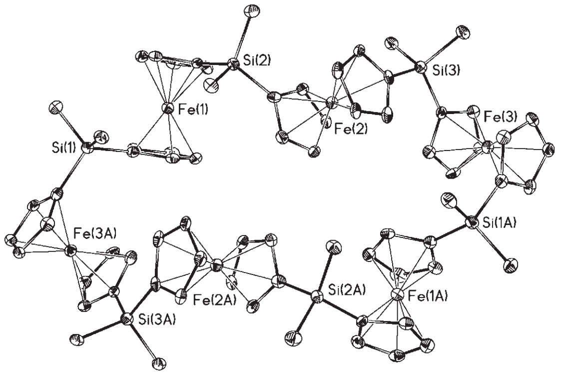
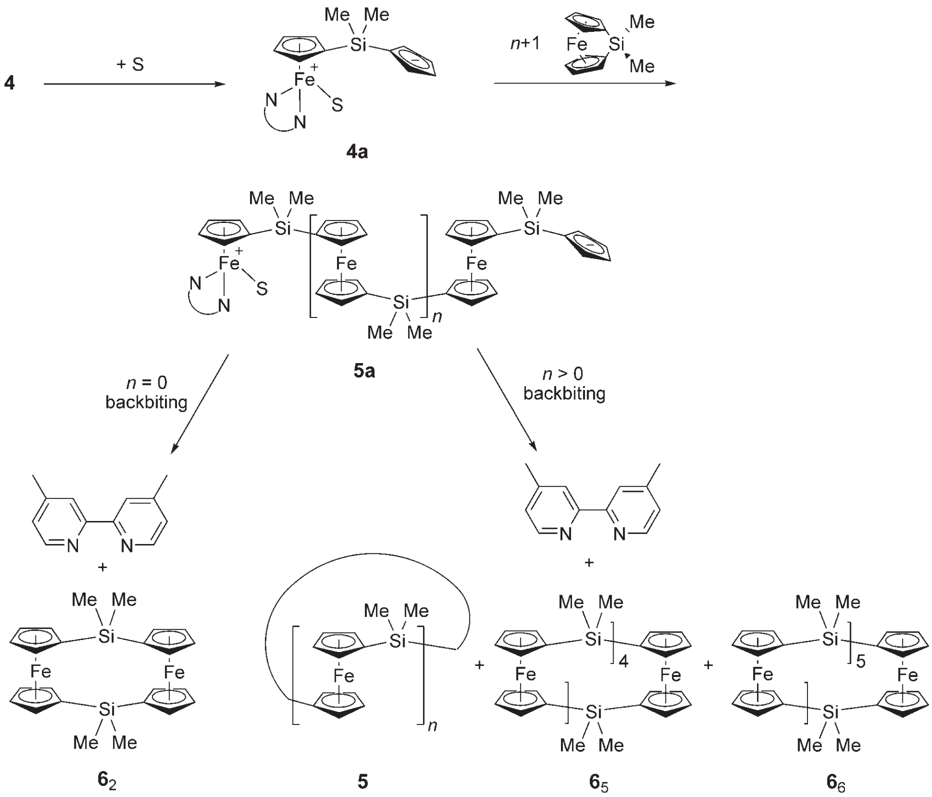


Figure 2. Molecular structure of $\mathbf{6}_6$. Thermal ellipsoids are set at the 30% probability level; hydrogen atoms have been removed for clarity.

Single crystal X-ray diffraction studies were performed to confirm the structures of cyclic oligomers $\mathbf{6}_5$ and $\mathbf{6}_6$ (Figures 1 and 2).[16] The Fe–C and Si–C bond distances in $\mathbf{6}_5$ and $\mathbf{6}_6$ are similar to those of previously reported linear oligoferrocenylsilanes.[18–20] The intramolecular Fe···Fe separations in $\mathbf{6}_5$ range from 5.9038(7) Å [d(Fe(1)···Fe(2))] to 6.3426(7) Å [d(Fe(5)···Fe(1))], and the corresponding distances in $\mathbf{6}_6$ range from 5.6395(17) Å [d(Fe(2)···Fe(3))] to 6.1069(18) Å [d(Fe(1)···Fe(2))]. These iron–iron distances are comparable to those in the linear oligoferrocenylsilanes.[18–20]

Analysis of the isolated PFS **5** by gel permeation chromatography (GPC) gave an estimate of $M_n = 11\,900$ and PDI = 2.12 (M_n = number-average molecular weight, PDI = polydispersity index) versus polystyrene standards. As it seemed highly likely that this material was also cyclic, we studied its microstructure by MALDI-TOF mass spectrometry.[21] This experiment confirmed the cyclic nature of PFS **5** (Figure 3). Only peaks that are integer multiples of the molecular weight of **1** were present, indicating a lack of end groups in the polymer. Interestingly, two populations of PFS **5** with different average chain lengths were observed, which presumably arise from backbiting and chain extension reactions that disrupt chain propagation in a random fashion (Scheme 1).

Scheme 1 illustrates a possible mechanism for the photolysis of ferrocenophane **1** in the presence of a stoichiometric amount of Me_2bpy. The formation of polymeric products **5** in this reaction indicated that chain propagation is faster than the initiation of ferrocenophane **1**. After initial Me_2bpy coordination and Cp ring slippage to give **4** (not observed), the η^1-coordinated Cp ring dissociates from the iron center (**4a**, not observed), and the free Cp anion induces rapid chain propagation to yield polymer **5a**. The $[CpFe(Me_2bpy)S]^+$ end group of PFS **5a** is likely unstable, and the pendent Cp anion can attack the iron center in the other end group in a backbiting reaction. This process releases Me_2bpy and yields cyclic oligoferrocenylsilanes of various ring sizes. Compared to the photolysis of ferrocenophane **1** in the presence of dppe,[11] the propensity for backbiting during



Scheme 1. Possible mechanism for the photolysis of ferrocenophane **1** in the presence of Me_2bpy. S = solvent, $\widehat{NN}$ = Me_2bpy.

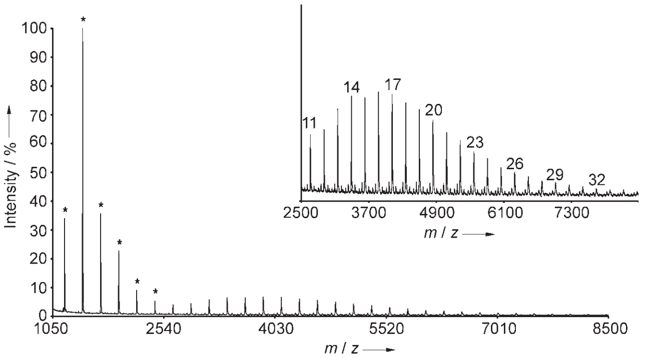


Figure 3. MALDI-TOF mass spectrum of PFS **5**. The asterisks indicate the lower-molecular-weight population of polymer chains. The inset contains the spectrum for the higher-molecular-weight population; the number above each peak corresponds to the degree of polymerization for that oligomer.

chain growth in the Me_2bpy reaction is presumably a consequence of the weaker binding strength of Me_2bpy at the soft Fe^{II} center.

Cyclic oligoferrocenylsilanes are also useful electrochemical models to explain the two-wave redox behavior of the PFS high polymer in cyclic voltammetry. Our previous work on linear oligoferrocenylsilanes is fully consistent with the following explanation: oxidation of the Fe^{II} centers to Fe^{III} initially occurs at alternating iron sites along the chain, and the remaining sites are oxidized at a higher potential.[18] We were therefore interested in comparing the electrochemical properties of cyclic oligomers $\mathbf{6}_5$ and $\mathbf{6}_6$ to those of the linear oligomers. The results of cyclic voltammetry experiments are given in Figure 4 and in Table S1 in the Supporting Information.

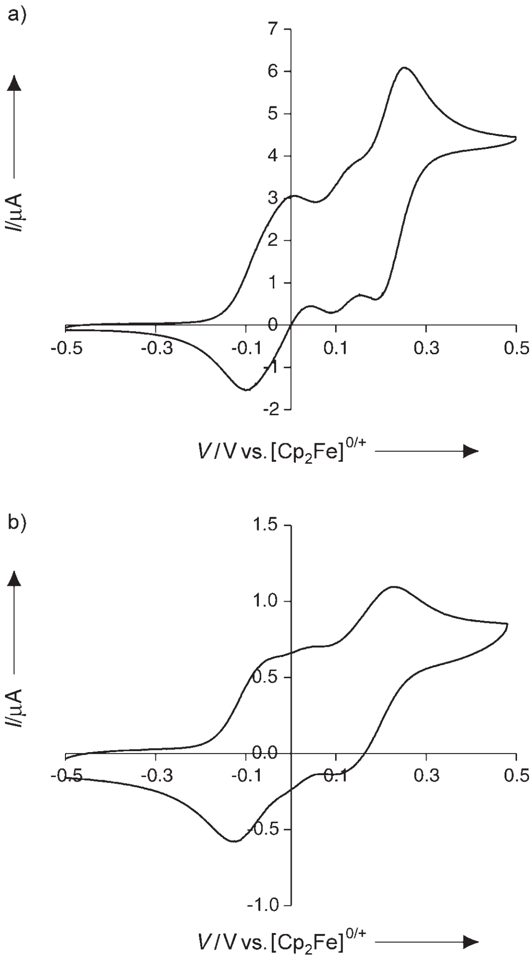
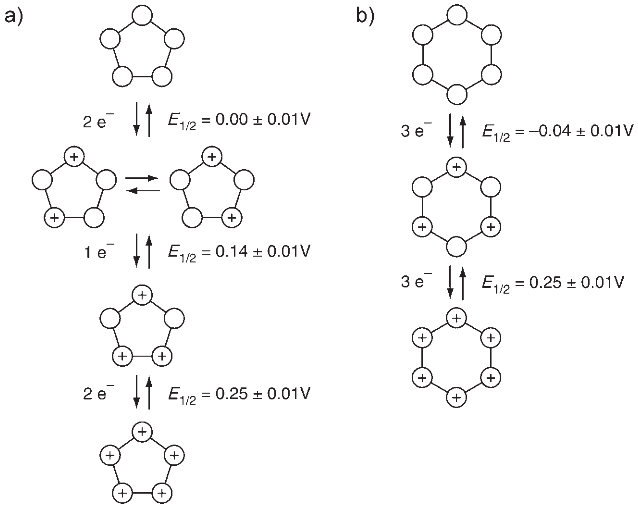


Figure 4. Cyclic voltammograms of a) cyclic pentamer $\mathbf{6}_5$ and b) cyclic hexamer $\mathbf{6}_6$ at a scan rate of 25 mVs^{-1}. A 1:1 mixture of CH_2Cl_2 and CH_3CN was used as solvent and $[NBu_4][PF_6]$ was the supporting electrolyte.

The electrochemical behavior of cyclic pentamer $\mathbf{6}_5$ and cyclic hexamer $\mathbf{6}_6$ are consistent with the proposed model (Scheme 2).[18] As anticipated, we observed three waves with an approximate ratio of 2:1:2 for the odd-numbered cyclic oligomer ($\mathbf{6}_5$) and two waves with an approximate ratio of 1:1 for the even-numbered cyclic oligomer ($\mathbf{6}_6$). The differences between the first and last oxidation potentials for each cyclic oligomer, 0.27 ± 0.02 V, agree with reported values for linear analogues.[18] This agreement suggests that the values of the initial and final potentials do not depend on the number of intervening redox events.



Scheme 2. a) Redox behavior of cyclic pentamer $\mathbf{6}_5$. b) Redox behavior of cyclic hexamer $\mathbf{6}_6$. Each circle represents a ferrocene unit; potentials are given relative to $[Cp_2Fe]^{0/+}$.

Significantly, performing the photolysis of ferrocenophane **1** and Me_2bpy in THF for 2 h at a lower temperature (5 °C rather than 35 °C) leads to substantially higher yields of polymer **5** (ca. 54 % relative to cyclic oligomers) with higher molecular weights ($M_n = 28\,400$, PDI = 1.46). This result suggests that our new method offers unprecedented opportunities to access cyclic PFS with different molecular weights; this protocol may also be applicable to other related strained metallorings containing other metals, π-hydrocarbon ligands, and bridging groups.[5b] We are currently examining other bidentate ligands to access higher homologues of oligoferrocenylsilanes $\mathbf{6}_x$.

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[1] *Cyclic Polymers*, 2nd ed. (Ed.: J. A. Semlyen), Kluwer Academic Publishers, Dordrecht, **2000**.

[2] C. W. Bielawski, D. Benitez, R. H. Grubbs, *Science* **2002**, *297*, 2041–2044.

[3] M. Tamm, A. Kunst, E. Herdtweck, *Chem. Commun.* **2005**, 1729–1731.

[4] We have previously reported evidence that low-molecular-weight cyclic PFS ($M_n < 4700$) is formed from the very slow (1.5 day) reaction of **1** with a platinasila[2]ferrocenophane catalyst in the presence of BH_3·THF. See: K. Temple, A. J. Lough, J. B. Sheridan, I. Manners, *J. Chem. Soc. Dalton Trans.* **1998**, 2799–2806.

[5] a) D. A. Foucher, B.-Z. Tang, I. Manners, *J. Am. Chem. Soc.* **1992**, *114*, 6246–6248; b) D. E. Herbert, U. F. J. Mayer, I. Manners, *Angew. Chem.* **2007**, *119*, 5152–5173; *Angew. Chem. Int. Ed.* **2007**, *46*, 5060–5081; c) V. Bellas, M. Rehahn, *Angew. Chem.* **2007**, *119*, 5174–5197; *Angew. Chem. Int. Ed.* **2007**, *46*, 5082–5104.

[6] In this notation, the superscript refers to the degree of polymerization.

[7] a) D. L. Zechel, D. A. Foucher, J. K. Pudelski, G. P. A. Yap, A. L. Rheingold, I. Manners, *J. Chem. Soc. Dalton Trans.* **1995**, 1893–1899; b) Y. Ni, R. Rulkens, J. K. Pudelski, I. Manners, *Macromol. Rapid Commun.* **1995**, *16*, 637–641; c) J. Park, Y. Seo, S. Cho, D. Whang, K. Kim, T. Chang, *J. Organomet. Chem.* **1995**, *489*, 23–25; d) G. Calleja, F. Carré, G. Cerveau, P. Labbé, L. Coche-Guérente, *Organometallics* **2001**, *20*, 4211–4215; e) A. Berenbaum, A. J. Lough, I. Manners, *Organometallics* **2002**, *21*, 4415–4424.

[8] For selected recent examples of [1.1]ferrocenophanes containg other bridging atoms, see: H. Brunner, J. Klankermayer, M. Zabel, *J. Organomet. Chem.* **2000**, *601*, 211–219; W. Uhl, I. Hahn, A. Jantschak, T. Spies, *J. Organomet. Chem.* **2001**, *637–639*, 300–303; A. Althoff, P. Jutzi, N. Lenze, B. Neumann, A. Stammler, H.-G. Stammler, *Organometallics* **2002**, *21*, 3018–3022; M. Scheibitz, R. F. Winter, M. Bolte, H.-W. Lerner, M. Wagner, *Angew. Chem.* **2003**, *115*, 954–957; *Angew. Chem. Int. Ed.* **2003**, *42*, 924–927; H. Braunschweig, C. Burschka, G. K. B. Clentsmith, T. Kupfer, K. Radacki, *Inorg. Chem.* **2005**, *44*, 4906–4908; J. A. Schachner, G. A. Orlowski, J. W. Quail, H.-B. Kraatz, J. Müller, *Inorg. Chem.* **2006**, *45*, 454–459.

[9] Carbon-bridged [1^n]ferrocenophanes ($n = 2$–5) and mixed carbon-bridged [1^4]metallocenophanes containing ferrocene, ruthenocene, or cobaltocenium units have been reported in low yields. See: U. T. Mueller-Westerhoff, *Angew. Chem.* **1986**, *98*, 700–716; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 702–717, and references therein.

[10] Köhler and co-workers prepared a cyclic compound containing seven ferrocene units with adjacent Cp rings doubly bridged by two $-SiMe_2-$ groups. Although not a [1^n]ferrocenophane, it was the largest known cyclic ferrocene oligomer at the time. See: B. Grossmann, J. Heinze, E. Herdtweck, F. H. Köhler, H. Nöth, H. Schwenk, M. Spiegler, W. Wachter, B. Weber, *Angew. Chem.* **1997**, *109*, 384–386; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 387–389.

[11] M. Tanabe, S. C. Bourke, D. E. Herbert, A. J. Lough, I. Manners, *Angew. Chem.* **2005**, *117*, 6036–6040; *Angew. Chem. Int. Ed.* **2005**, *44*, 5886–5890.

[12] For work on Fe–Cp bond-cleavage reactions in phosphorus-bridged [1]ferrocenophanes, see: T. Mizuta, Y. Imamura, K. Miyoshi, *J. Am. Chem. Soc.* **2003**, *125*, 2068–2069.

[13] a) M. Tanabe, I. Manners, *J. Am. Chem. Soc.* **2004**, *126*, 11434–11435; b) M. Tanabe, G. W. M. Vandermeulen, W. Y. Chan, P. W. Cyr, L. Vanderark, D. A. Rider, I. Manners, *Nat. Mater.* **2006**, *5*, 467–470.

[14] We have recently explored the analogous chemistry with terpyridine ligands, and the results are very different, see: W. Y. Chan, A. J. Lough, I. Manners, *Chem. Eur. J.* **2007**, DOI: 10.1002/chem.200700420.

[15] The degree of polymerization for each oligoferrocenylsilane is indicated by a subscript in its compound number. For example, $\mathbf{6}_2$ refers to the cyclic dimer disila[1.1]ferrocenophane.

[16] See the Supporting Information for full experimental details.

[17] The reaction mixture contains PFS **5** and various cyclic oligoferrocenylsilanes in approximately the following amounts (determined from integrations of the methyl signals in the ^1H NMR spectrum, average of three experiments): PFS **5** 24%, cyclic dimer $\mathbf{6}_2$ 17%, cyclic pentamer $\mathbf{6}_5$ 21%, cyclic hexamer $\mathbf{6}_6$ 9%.

[18] R. Rulkens, A. J. Lough, I. Manners, S. R. Lovelace, C. Grant, W. E. Geiger, *J. Am. Chem. Soc.* **1996**, *118*, 12683–12695.

[19] A. J. Lough, I. Manners, R. Rulkens, *Acta Crystallogr. Sect. C* **1994**, *50*, 1667–1669.

[20] K. H. Pannell, V. V. Dementiev, H. Li, F. Cervantes-Lee, M. T. Nguyen, A. F. Diaz, *Organometallics* **1994**, *13*, 3644–3650.

[21] It is known that the most probable molecular weights obtained by MALDI-TOF MS and GPC only show good agreement for polymers with a narrow molecular weight distribution (PDI < 1.1). For more polydisperse polymers, the most probable molecular weight obtained by MALDI-TOF MS is significantly lower than that obtained from GPC measurements. For details, see M. W. F. Nielen, *Mass Spectrom. Rev.* **1999**, *18*, 309–344, and references therein.