Development of an Easy-to-Use Mass Spectrometric Technique to Monitor Solid-Phase Reactions on Polystyrene Supports

Katja Heinze,* Ute Winterhalter, and Thomas Jannack[a]

Abstract: By using mass spectrometry as an analytical tool to characterise substituted, cross-linked polystyrene resins, it is possible to directly monitor the progress of the solid-phase reactions performed on these resins without prior cleavage of the resin-bound molecules. Therefore, this is a true on-resin analytical method. The mass-to-charge ratios observed in the mass spectra are readily assigned to fragments of the polymer that include the chemically bound substituents. This is the first time that the formation and breaking of bonds have been directly observed on the polymeric support. Furthermore, the relative intensities of the signals in the mass spectra provide a measure of the completeness of the reaction. Because these measurements are rapidly performed without further chemical transformations or cleavage procedures, and because only minimal amounts of material are needed, this technique could become the solid-phase equivalent of thin-layer chromatography used in classical liquid-phase chemistry.

Keywords: IR spectroscopy · kinetics · mass spectrometry · polystyrene · solid-phase synthesis

Introduction

Within the space of a few years, combinatorial synthesis has become a major tool to find and optimise important structures in pharmaceutically active compounds.[1] This led to a renaissance of solid-phase organic synthesis (SPOS), which has distinct advantages over classic liquid-phase synthetic methods.[2] To fully exploit the potential of SPOS the reactions performed must go to completion, preferably at a high rate. A major hindrance to reaching this goal is the lack of simple analytical methods to establish the identity of the product from a solid-phase reaction directly on the resin and—even more difficult—to monitor the course of a solid-phase reaction (real-time monitoring). Within the methods used so far for resin-bead analysis, such as NMR[3a–k], XPS[3l] and IR spectroscopy[4] in particular single-bead FT-IR spectroscopy has proven valuable, because only a minimal amount of material and time is required for analysis. Of course, only reactions that involve either starting materials or products that possess readily detectable and identifiable IR absorption bands, such as those that arise from carbonyl or hydroxyl stretch vibrations, can be monitored.

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We report here a novel, direct mass spectrometric method[5] to characterise resin-bound functionalities and molecules, and for real-time monitoring of the progress of solid-phase reactions performed on cross-linked polystyrene. The validity of this method is checked against the well-established IR method,[4] if this was applicable.

Results and Discussion

Preparation and characterisation of functionalised polystyrene resins: In the course of our studies on solid-phase reactions we employed the well-known silyl ether linker,[6] which allows the retrieval of the final product from the resin by fluoridolysis. Scheme 1 shows the reaction sequence that has been performed on the cross-linked polystyrene resins and Table 1 lists the functionalised polystyrene resins prepared in this study. Swellable polystyrene resins with 2% divinyl benzene (DVB) or highly cross-linked resins with 20% DVB were employed for comparison.

The attachment of the silyl chloride linker group through bromination and lithiation steps (Scheme 1: Reactions I and II, respectively) has already been thoroughly investigated.[7] This linker group has been used for the solid-phase synthesis of, for example, oligosaccharides[6a,b] and prostaglandins.[6c] It has been found that the two-step procedure of bromination and lithiation is superior to direct lithiation with *n*BuLi/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA)[8] with respect to the reproducibility, control of the degree of function-

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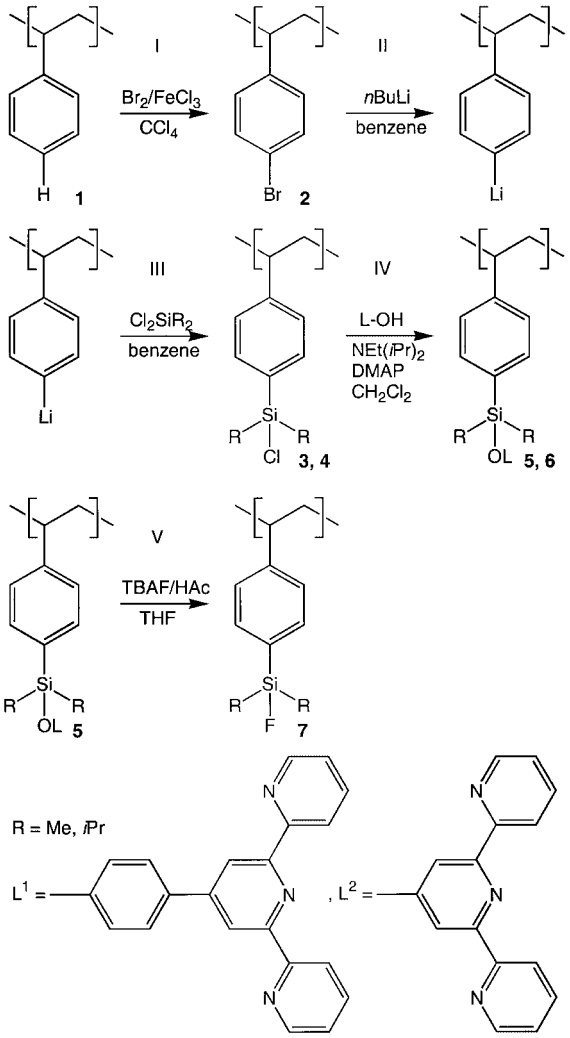

Scheme 1. Reaction sequence performed on the cross-linked polystyrene resins.

Table 1. Polystyrene resins.

	DVB [%][a]	Functional group[b]	Loading [mmol g^{-1}][c]
1a	2	H	–
1b	20	H	–
2a-1.2	2	Br	1.22
2a-2.6	2	Br	2.61
2a-5.7	2	Br	5.69
2b-3.2	20	Br	3.24
3	2	Si(*i*Pr)$_2$Cl	n.d.
4	2	Si(Me)$_2$Cl	n.d.
5-0.16	2	Si(*i*Pr)$_2$OL^1	0.16
5-0.23	2	Si(*i*Pr)$_2$OL^1	0.23
5-0.24	2	Si(*i*Pr)$_2$OL^1	0.24
5-0.46	2	Si(*i*Pr)$_2$OL^1	0.46
6	2	Si(*i*Pr)$_2$OL^2	n.d.
7	2	Si(*i*Pr)$_2$F	n.d.
8	2	Si(*i*Pr)$_2$OH	n.d.

[a] DVB = divinylbenzene. [b] L^1 and L^2 are the terpyridines shown in Scheme 1. [c] Determined by elemental analysis; n.d. = not determined.

alisation and homogeneity of the resin.[7b] Therefore, we investigated the two-step procedure.

The influence of the degree of cross-linking of the starting polystyrene (**1a** and **1b** with 2 and 20% DVB, respectively) was also investigated. While from the low cross-linked resin **1a** slightly coloured, homogenous materials **2a** were obtained that could be metalated in a single step, the highly cross-linked polystyrene **1b** gave a more intensely coloured product **2b**-3.2 (the number 3.2 refers to the loading of the resin in mmol g^{-1}), which could not be completely lithiated (see below). This is probably the consequence of the poorer swelling properties of **2b**-3.2 that prevents sufficient penetration of the reagent. This material was therefore not investigated further.

The resins **3** and **4** (Scheme 1: reaction III), which contain silyl chloride, were obtained from the lithiated polymer by quenching with dimethyldichlorosilane and diisopropyldichlorosilane, respectively. These silylated polymers were treated with the hydroxyl-substituted terpyridines L^{1}OH and L^{2}OH (Scheme 1: reaction IV) in dichloromethane and Hünig's base under (dimethylamino)pyridine (DMAP) catalysis to give the dialkylsilyl-linked terpyridine-polymer constructs **5** and **6**. The systems derived from **3** (R = *i*Pr) gave much better results and higher loadings than those derived from **4** (R = Me), so that we concentrated on the former resins. A similar result has been reported by Danishefsky et al., who described the superior performance of the isopropyl-substituted resin (R = *i*Pr) relative to the phenyl-substituted analogue (R = Ph).[6a]

Cleavage of the silyl ether linkage was accomplished by fluoridolysis with tetra-*n*-butylammonium fluoride (TBAF) and acetic acid in THF (Scheme 1: reaction V) to give the terpyridine L^{1}OH and the residual polymer **7** containing silyl fluoride.

All polystyrene resins prepared (Table 1) were analysed by IR spectroscopy (CsI pellets) and mass spectrometry (EI-MS). Resins **1**, **2** and **5** were also characterised by elemental analysis to give the final loading of bromine (resins **2**) and terpyridine (resins **5**). IR spectroscopy was only helpful for Reactions III – V and resins **3** and **5**, as only in these cases are useful IR absorptions present (**3**: $\tilde{\nu} = 883$ cm^{-1}; **5**: $\tilde{\nu}_{\text{pyridine}} = 1514$ cm^{-1}). For the brominated resins **2** the absorption from the C–Br stretch at $\tilde{\nu} = 1011$ cm^{-1} is too weak and overlaps with bands of the polystyrene backbone. Therefore, a new technique is clearly needed to examine these resins and reactions. We investigated the mass spectrometric characteristics (ionisation method: EI, heating rate: 5 K s^{-1}, 70 eV, see the Experimental Section) of resins **1** – **7** (Table 1).

Figure 1 shows the ion current at *m*/*z* 104, which parallels the total ion current, plotted against the temperature for resin **1a**. All investigated polystyrene-based resins show a similar current versus temperature profile. The mass spectrum of **1a** at a temperature above 400 °C is shown in Figure 2. The base peak at *m*/*z* 104 corresponds to a C_8H_8 fragment, as confirmed by the correct isotopic distribution. It is assigned to monomeric styrene which arises from depolymerisation of the polystyrene at elevated temperatures.[9] This endothermal decomposition process is also confirmed by thermogravimetric measurements and differential scanning calorimetry (see the Experimental Section and the Supporting Information). The less intense signals at *m*/*z* 207 and 312 are assigned to the quasi-molecular ions $[C_{16}H_{15}]^+$ (styrene dimer minus a hydrogen) and $[C_{24}H_{24}]^+$ (styrene trimer), respectively.

0947-6539/00/0622-4204 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 22

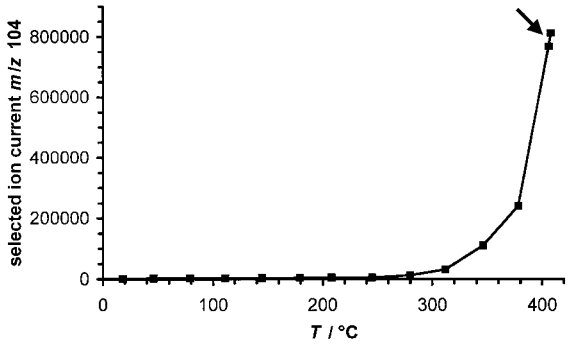

Figure 1. Selected ion current (m/z 104) of resin **1a**.

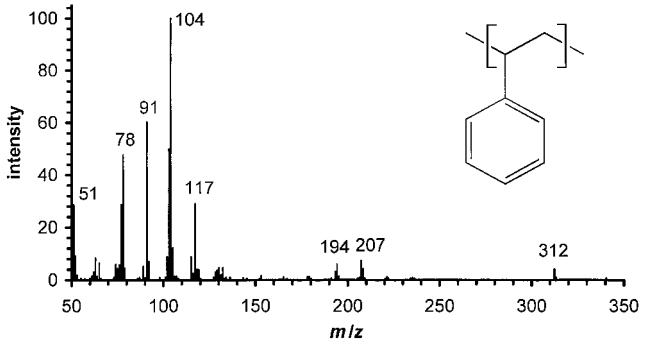

Figure 2. EI mass spectrum of polystyrene resin **1a** at 408 °C.

For the brominated resins **2** additional peaks at m/z 169, 182, 249 and 262 were observed; these are assigned to the brominated fragments $[C_7H_6Br]^+$, $[C_8H_7Br]^+$, $[C_7H_5Br_2]^+$ and $[C_8H_6Br_2]^+$, respectively (Figure 3). Again, all signals show

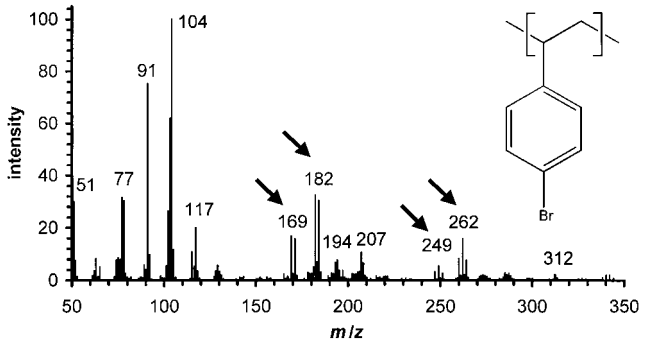

Figure 3. EI mass spectrum of brominated polystyrene resin **2a**-2.6 at 406 °C.

the correct isotopic distribution. From the mass spectrometric data it is not clear whether the disubstituted fragments were present in the resin before heating or were generated within the MS experiment. In the literature it has been proposed that bromination takes place exclusively at the *para* positions.[7b] A further indication that indeed more than one bromine per aromatic ring can be introduced is given by the elemental analysis of resin **2a**-5.7, which has a higher bromine content than that expected for a monosubstitution of all aromatic rings (the analysis indicates a mono-to-disubstition ratio of 12:1).

The EI mass spectrum of the silyl chloride resin **3**, derived from the brominated resins **2a**, is shown in Figure 4. Evidently all peaks corresponding to the starting material **2a** have

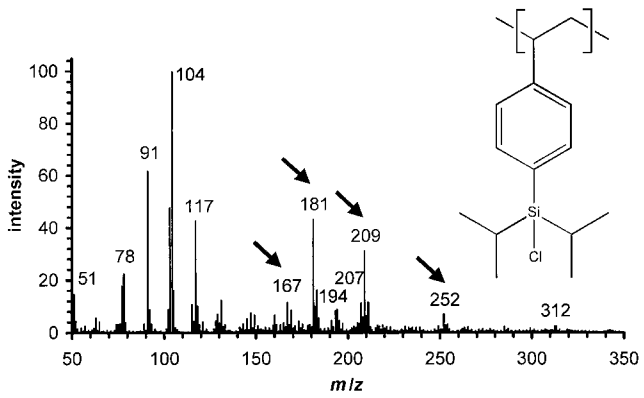

Figure 4. EI mass spectrum of polystyrene resin **3** at 406 °C.

disappeared, while new peaks at m/z 167, 181, 209 and 252 have emerged. These last correspond to the fragment ions $[C_8H_7Si(iPr)_2Cl - 2\,iPr+H]^+$ ($[C_8H_8SiCl]^+$), $[C_8H_7Si(iPr)_2Cl - iPr - C_2H_4]^+$ ($[C_9H_{10}SiCl]^+$), $[C_8H_7Si(iPr)_2Cl - iPr]^+$ ($[C_{11}H_{14}SiCl]^+$) and $[C_8H_7Si(iPr)_2Cl]^+$ ($[C_{14}H_{21}SiCl]^+$), respectively (Table 2). This assignment is based on the correct isotopic

Table 2. Characteristic peaks (m/z) of diisopropylsilyl-substituted resins **3**, **5**, **6**, **7** and **8**

	[M – X][a]	[M – X – *i*Pr]	[M – X – *i*Pr – C_2H_4]	[M – X – 2*i*Pr+H]
3 (X = Cl)	252	209	181	167
5 (X = L^1)	541	498	470	456
6 (X = L^2)	465	422	394	380
7 (X = F)	236	193	165	151
8 (X = OH)	234	191	163	149

[a] M = $C_8H_7Si(iPr)_2$.

patterns of the signals and has also been corroborated by the preparation and mass spectrometric characterisation of the analogous dimethylsilylchloride resin **4** (see the Experimental Section).

Formation of the L^1 terpyridine silyl ether gave polymer **5** (Scheme 1: reaction IV). Its EI mass spectrum (Figure 5) displays intense peaks at m/z 541, 498, 470 and 456, which are assigned by analogy to the those of polymer **3** as $[C_8H_7Si(iPr)_2OL^1 - 2\,iPr+H]^+$ ($[C_{29}H_{22}N_3OSi]^+$), $[C_8H_7Si(iPr)_2OL^1 - iPr - C_2H_4]^+$ ($[C_{30}H_{24}N_3OSi]^+$), $[C_8H_7Si(iPr)_2OL^1 - iPr]^+$ ($[C_{32}H_{28}N_3OSi]^+$) and $[C_8H_7Si(iPr)_2OL^1]^+$ ($[C_{35}H_{35}N_3OSi]^+$) (Table 2). A similar result has been obtained for the L^2-substituted resin **6** (see the Experimental Section) providing further proof of the proposed assignments.

After cleavage of the terpyridine moiety L^1OH from the resin with TBAF/HAc, the silyl fluoride resin **7** was obtained (Scheme 1: reaction V). Its EI mass spectrum displays signals at m/z 151, 165, 193 and 236, which are assigned to the fragment ions $[C_8H_7Si(iPr)_2F - 2\,iPr+H]^+$ ($[C_8H_8SiF]^+$), $[C_8H_7Si(iPr)_2F - iPr - C_2H_4]^+$ ($[C_9H_{10}SiF]^+$), $[C_8H_7Si(iPr)_2F - iPr]^+$ ($[C_{11}H_{14}SiF]^+$) and $[C_8H_7Si(iPr)_2F]^+$ ($[C_{14}H_{21}SiF]^+$), respectively (Table 2).

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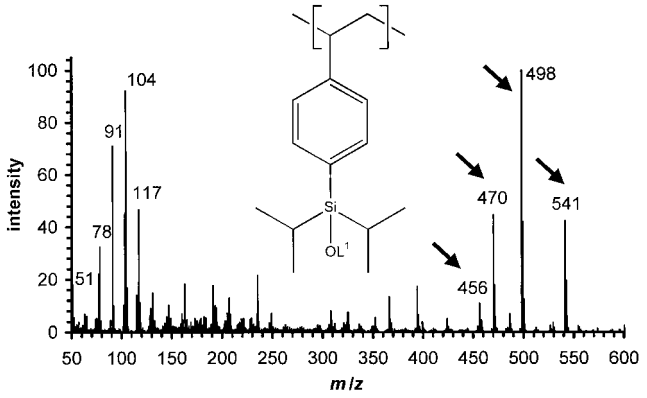


Figure 5. EI mass spectrum of polystyrene resin **5**-0.46 at 405 °C.

From Table 2 it is evident that all investigated polystyrene resins with a diisopropylsilyl group undergo the same fragmentation pattern, namely the loss of C_3H_7 and C_2H_4 fragments. This fragmentation is independent of the substituent X at the silicon atom (X = Cl, L^1, L^2, F, OH; Table 2).

Thus, the data obtained proves that mass spectrometry is useful for the characterisation of substituted polystyrene resins. Additionally, this method allows for the first time to "see" bond formation and bond breaking processes directly—undisturbed by non-bound material—on the resin.

Quantification of resin loading with IR spectroscopy and mass spectrometry: Further investigations showed that not only the characteristic peaks of substituted polystyrene resins can be detected in the EI mass spectrum, but also that the intensities of these peaks relative to the intensity of the styrene peak at *m*/*z* 104 are correlated with the loading of the resin. For the brominated resins **2** (see the Experimental Section and Supporting Information), a linear correlation of the relative intensity of *m*/*z* 182 (relative to the intensity of the typical peak at *m*/*z* 104) with the bromine loading was found with $R^2 = 0.9939$. Such a correlation was not possible with IR spectroscopy as the only distinct difference in the vibration pattern of resins **2** compared with resins **1** is the C–Br stretch at $\tilde{\nu} = 1011\ cm^{-1}$, which has a very low intensity so that a reliable integration was not achieved.

For the terpyridine resins **5** such a correlation was possible by both IR spectroscopicy and the mass spectrometry. Figure 6 shows the correlation obtained from mass spectrometry

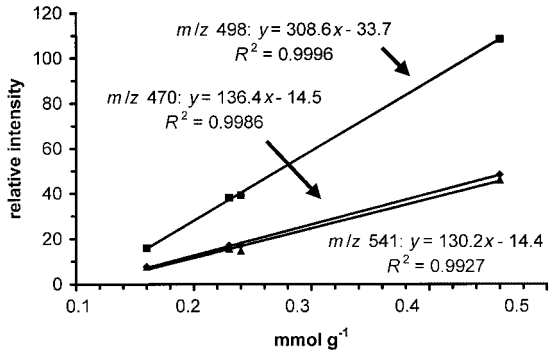


Figure 6. Correlation of loading of resins **5** with peak intensities (*m*/*z* 541, 498, 470 relative to *m*/*z* 104).

(relative intensities of typical peaks at *m*/*z* 470, 498 and 541 versus loading of the resin with terpyridine). Figure 7 depicts the IR spectroscopic correlation $[\int(\tilde{\nu} = 1514\ cm^{-1})/\int(\tilde{\nu} = 1494\ cm^{-1})$ plotted against the loading of the resin with terpyridine; the absorption at $\tilde{\nu}$ 1514 cm^{-1} is characteristic for terpyridine and the absorption at 1494 cm^{-1} is characteristic

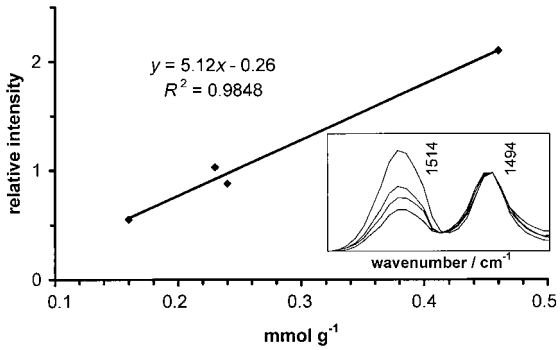
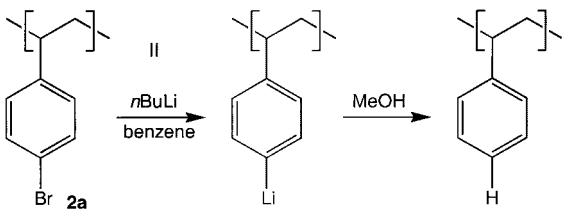


Figure 7. Correlation of loading of resins **5** with IR band intensity $[\int(\tilde{\nu} = 1514\ cm^{-1})$ relative to $\int(\tilde{\nu} = 1494\ cm^{-1})]$. Inset: IR spectra of **5**.

for polystyrene[4c]]. Satisfying correlations (Figures 6 and 7) were obtained with both methods. These results provided the basis for a quantitative examination of the reactions performed on the polystyrene resins (Scheme 1).

Monitoring the progress of solid-phase reactions: The bromination (Scheme 1; reaction I) was carried out as described in the literature with $FeCl_3$ as the catalyst. After the indicated times (30, 60, 120, 240, 360 and 1440 min) one drop of the suspension was removed by pipette, and then quickly washed and dried.[7b] These resin beads were subjected to EI mass spectrometric analysis under the same experimental conditions (heating rate, final temperature, amplification, peak focusing). The relative intensity of the characteristic peak of brominated polystyrene resins (*m*/*z* 182) increased (see the Supporting Information). The data were fit by a pseudo-first-order rate equation (see the Experimental Section) to obtain a rate constant of $k = 2.8 \times 10^{-4}\ s^{-1}$, which indicated that the reaction is complete after 6 h.

The lithiation step (Scheme 1: reaction II) was monitored in a similar manner; a few of the lithiated beads were removed by pipette, quenched with methanol (Scheme 2), washed, dried and analysed. The reaction proceeded rapidly, as seen by the rapid decrease of the peaks associated with the brominated resins (*m*/*z* 182 and 169) and was completed after 2–3 h.

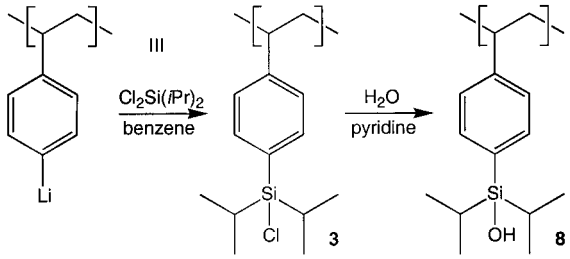


Scheme 2. Lithiation of the brominated polymer and subsequent methanolysis.

0947-6539/00/0622-4206 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 22

For resin **2a**-5.7 this reaction was incomplete under the applied conditions, as judged by the remaining peaks at *m*/*z* 182 and 169 after 24 h reaction time. This is probably caused by the poor swelling characteristics of this highly loaded resin which prevents sufficient penetration of the reagent. The same observation has been made for the highly cross-linked resin **2b**-3.2. A possible explanation might be that the high degree of cross-linking shields the bromine groups from the attack of the reagent.[10]

Quenching of the lithiated polymer with diisopropyldichlorosilane (Scheme 1: reaction III) to give resin **3** has been monitored by IR spectroscopy and mass spectrometry. Again, beads were removed from the reaction suspension, the silyl chloride **3** was hydrolysed with pyridine/water to the silanol **8** for analytical purposes (Scheme 3) and finally the resin beads were dried and analysed.



Scheme 3. Silylation of the lithiated polymer and subsequent hydrolysis to **8**.

A new distinct absorption band at $\tilde{\nu} = 883\ \mathrm{cm^{-1}}$ was observed in the IR spectrum of **8**. The area under this absorption was measured relative to the area under the polystyrene absorption band at $\tilde{\nu} = 1494\ \mathrm{cm^{-1}}$ and this data was plotted against time (Figure 8). The fit to a pseudo-first-order rate equation gave $k = 8.3 \times 10^{-4}\ \mathrm{s^{-1}}$.

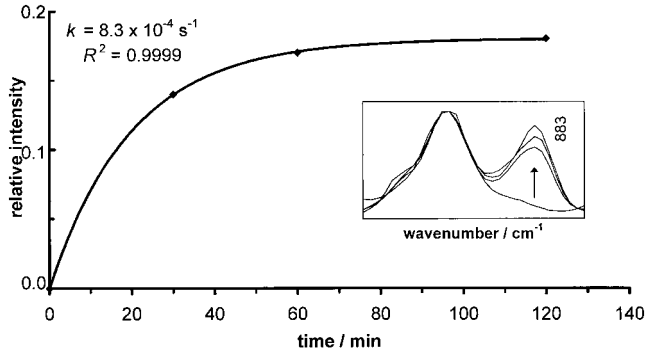


Figure 8. IR spectra (inset) and time course for reaction III.

The mass spectrometrical analysis (Figure 9), based on the peaks at *m*/*z* 163, 191 and 234 (which correspond to $[C_8H_7Si(i\mathrm{Pr})_2OH - 2\,i\mathrm{Pr} + H]^+$ ($[C_8H_8SiOH]^+$), $[C_8H_7Si(i\mathrm{Pr})_2OH - i\mathrm{Pr} - C_2H_4]^+$ ($[C_9H_{10}SiOH]^+$), $[C_8H_7Si(i\mathrm{Pr})_2OH - i\mathrm{Pr}]^+$ ($[C_{11}H_{14}SiOH]^+$) and $[C_8H_7Si(i\mathrm{Pr})_2OH]^+$ ($[C_{14}H_{21}SiOH]^+$), respectively; Table 2) gave $k = (10-14) \times 10^{-4}\ \mathrm{s^{-1}}$, which is in satisfactory agreement with the IR data.

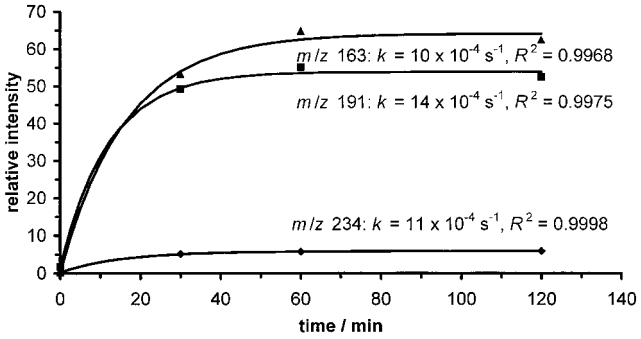


Figure 9. Time course for reaction III.

It was possible to monitor the reaction of L^1OH with the silyl chloride resin **3** (Scheme 1: reaction IV) with both IR spectroscopy (Figure 10; increasing absorption band at $\tilde{\nu} = 1514\ \mathrm{cm^{-1}}$; see above) and by MS methods (Figure 11;

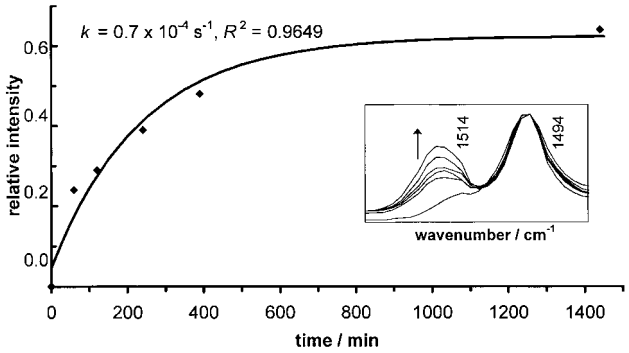


Figure 10. IR spectra (inset) and time course for reaction IV.

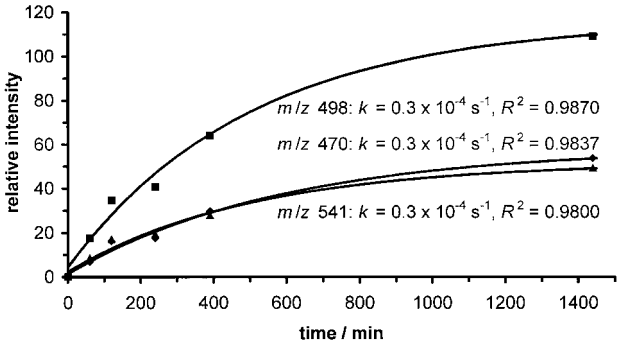


Figure 11. Time course for reaction IV.

increasing peaks at *m*/*z* 470, 498 and 541, see above). In both cases, a rather small rate constant was determined (IR: $k = 0.7 \times 10^{-4}\ \mathrm{s^{-1}}$; MS: $k = 0.3 \times 10^{-4}\ \mathrm{s^{-1}}$). For ester formation on polystyrene resins approximately tenfold larger rate constants have been determined by IR spectroscopy ($k = 2-6 \times 10^{-4}\ \mathrm{s^{-1}}$).[4b,e,f] The slow rate observed in the case of the silyl ether formation with L^1OH might be attributable to the fact that L^1OH is only marginally soluble in common solvents thus imposing "doubly heterogeneous" reaction conditions.

Similar to the ether formation, the cleavage of the silyl ether with TBAF (Scheme 1: reaction V) was monitored by both methods. The reaction was complete after only 2–3 h. The decrease of the band at $\tilde{\nu} = 1514\ \mathrm{cm^{-1}}$ gave $k = 13 \times$

$10^{-4}\,s^{-1}$ (Figure 12). In the mass spectrometric method, the decrease of the signals of resin **5** (*m*/*z* 470, 498 and 541, see above) and the simultaneous increase of signals of the silyl

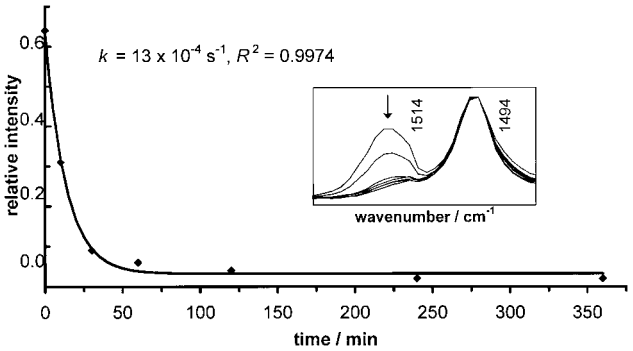


Figure 12. IR spectra (inset) and time course for reaction V.

fluoride resin **7** (*m*/*z* 165, 193 and 236, Table 2) were monitored and gave rate constants of $k = (12-13) \times 10^{-4}\,s^{-1}$ (decreasing) and $k = (5-10) \times 10^{-4}\,s^{-1}$ (increasing), respectively, in good agreement with the values determined by IR spectroscopy (Figure 13). The correlation coefficients (Fig-

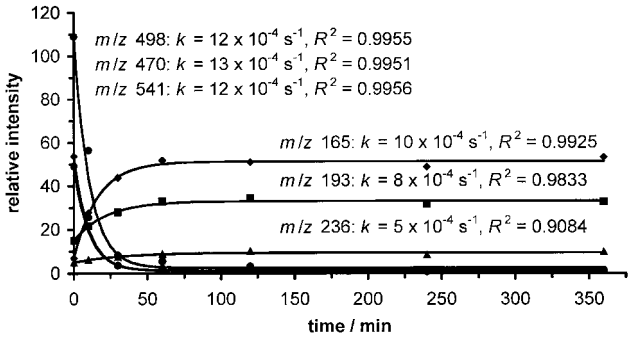


Figure 13. Time course for reaction V.

ure 13) as well as the better fit to the IR data show that the rate constants obtained from the decreasing signals are much more reliable than the constants obtained from the signals of the silyl fluoride resin **7**. This is most probably owing to the fact that the signals of resin **5** are much more intense than those of resin **7** and, therefore, give a much improved signal-to-noise ratio.

Conclusions

It has been shown that EI mass spectrometry is a readily available and powerful method to characterise functionalised polystyrene resins. It is not necessary to cleave the functionality to be analysed from the resin which would require a further reaction step. Unlike other methods, such as pellet FT-IR spectroscopy, elemental analysis, NMR spectroscopy or titration of functional groups, only minimal amounts of material (a few beads, or even a single bead) are required so that, in principle, a library of compounds (e.g. obtained by split and combine methods[1]) can be measured on a single bead. A further striking advantage is the fact that the signals observed by the MS method correspond exclusively to chemically bonded material and not to the sum of the chemically bonded and physically adsorbed material as determined by, for example, elemental analysis. Of course, because the depolymerisation of the polystyrene occurs only at elevated temperatures, functionalities which cannot withstand these condition cannot be analysed.

In addition to the characterisation of polystyrene polymers, a quantitative monitoring of the course of solid-phase reactions is possible; this allows the determination of the rate constants and, perhaps even more important, provides the practical chemist with a tool to answer the question as to whether a reaction takes place in the desired way and whether the reaction is complete or not. This is similar to TLC control used for usual liquid-phase reactions. EI mass spectrometry clearly can be used for this purpose.

Experimental Section

Polystyrene (2% and 20% DVB), $Cl_2Si(iPr)_2$, Cl_2SiMe_2, *n*BuLi in toluene, diisopropylethylamine, (dimethylamino)pyridine (DMAP) and $nBu_4NF \cdot 3H_2O$ (TBAF) were purchased from Fluka. The polystyrene resins were washed prior to use with NaOH, HCl, NaOH/dioxane, HCl/dioxane, H_2O and DMF at 60 °C and HCl/MeOH, H_2O, MeOH, MeOH/CH_2Cl_2 (1:3), MeOH/CH_2Cl_2 (1:10) and CH_2Cl_2 at room temperature according to the procedure by Farrall and Fréchet[7b], dried under vacuum and characterised by elemental analyses. The terpyridines L^1OH[11] and L^2OH[12] were prepared according to literature procedures. Benzene, toluene, THF, CCl_4 and CH_2Cl_2 were dried by standard methods and distilled under argon prior to use. All other reagents were used as received. For the solid-phase reactions, a flask with a nitrogen inlet and a fritted glass filter of coarse porosity were used. These allow the addition and removal of reagents and solvents without exposure of the resin to atmosphere.

Elemental analyses were performed by the microanalytical laboratory of the Organic Chemistry Department, University of Heidelberg. IR spectra were recorded on a BioRad Excalibur FTS 3000 spectrometer with caesium iodide pellets. Data were collected with 4 wavenumber resolution. Sixty-four scans were averaged. EI mass spectra were recorded on a Finnigan MAT 8400 spectrometer (electron energy 70 eV, heating rate $5\,K\,s^{-1}$, resolution $R = m/\Delta m = 1600$). The dry samples (a few beads) were ground to a fine power prior to their introduction into the mass spectrometer. Differential scanning calorimetry measurements were carried out on a Mettler DSC 30 (heating rate $10\,K\,min^{-1}$, under Ar from 30–600 °C). Thermogravimetric measurements were carried out on a Mettler TC 15 (heating rate $10\,K\,min^{-1}$ under Ar from 30–800 °C).

Data treatment and analysis: IR spectra were normalised by making the areas under the polystyrene band at $\tilde{\nu} = 1494\,cm^{-1}$ equal. Mass spectra were normalised by making the intensities of the peak at *m*/*z* 104 (usually the base peak at temperatures above 380–400 °C) equal. The normalised intensities of typical peaks were then plotted against time. The data points, obtained by either IR or MS methods, were then fitted to a pseudo-first-order rate equation (reactant signal $= y_0 + e^{-kt}$ or product signal $= y_0 + 1 - e^{-kt}$) as derived by Yan et al.[4b] with a non-linear regression program, Sigma Plot for Windows Version 4.01 (Jandel Scientific, San Rafael, CA 94901; http://www.spss.com), on a PC computer.

Characterisation of polystyrene resins after washing and drying

Resin 1a: Elemental analysis calcd (%) for (C_8H_8): C 92.26, H 7.74; found: C 92.21, H 7.72; IR (CsI): $\tilde{\nu} = 3083$ (m), 3061 (m), 3026 (m), 3002 (w), 2922 (br), 2851 (m), 1944 (w), 1871 (w), 1803 (w), 1746 (w), 1602 (m), 1494 (m), 1453 (m), 1369 (br), 1329 (w), 1182 (w), 1155 (w), 1070 (w), 1030 (w), 908 (w), 763 (s), 697 cm^{-1} (s); MS (EI, 408 °C): *m*/*z* (%): 51 (29), 78 (48), 91 (60) $[C_7H_7]$, 104 (100) $[C_8H_8]$, 117 (29) $[C_9H_9]$, 130 (5), 132 (5), 194 (6), 207 (7) $[(C_8H_8)_2 - H]$, 312 (4) $[(C_8H_8)_3]$; DSC (peak maxima): 423 °C (endother-

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mal; $\Delta H = -0.91\ kJ\,g^{-1}$); TG (weight loss): 87.2% (368 °C), 12.8% (547 °C), < 0.1% residue.

Resin 1b: Elemental analysis calcd (%) for $(C_8H_8)_5(C_{10}H_{10})$: C 92.26, H 7.74; found: C 91.76, H 7.91; IR (CsI): $\tilde{\nu} = 3083$ (m), 3059 (m), 3026 (m), 3002 (w), 2939 (br), 2856 (m), 1943 (w), 1869 (w), 1802 (w), 1748 (w), 1602 (m), 1493 (m), 1453 (m), 1366 (br), 1329 (w), 1182 (w), 1155 (w), 1070 (w), 1029 (w), 990 (w), 966 (w), 904 (w), 830 (w), 799 (m), 759 (s), 701 cm^{-1} (s); MS (EI, 406 °C): *m/z* (%): 51 (21), 78 (40), 91 (31) $[C_7H_7]$, 104 (100) $[C_8H_8]$, 117 (33) $[C_9H_9]$, 130 (9), 132 (12), 194 (4), 207 (5) $[(C_8H_8)_2 - H]$, 312 (3) $[(C_8H_8)_3]$; DSC (peak maxima): 425 °C (endothermal; $\Delta H = -0.73\ kJ\,g^{-1}$); TG (weight loss): 72.0% (353 °C), 27.9% (544 °C), < 0.1% residue.

Bromination of polystyrene resins 1a and 1b: $FeCl_3$ (10 mg per g of resin) was added to a suspension of washed polystyrene resin (5–10 g) in CCl_4 (30–50 mL). The reaction mixture was stirred for 0.5 h, then bromine (0.2–1.0 mL; 0.6–3.1 g per g of resin) was added in one portion, depending on the desired substitution level[7b]. After the indicated times (30, 60, 120, 240, 360 and 1440 min), a few drops of the suspension were removed by pipette, washed with CCl_4, acetone, acetone/H_2O (2:1), acetone, benzene, MeOH, and CH_2Cl_2 until all washings were colourless. The residue was dried in vacuo and analysed by IR spectroscopy and EI-MS.[13] After stirring for 24 h at room temperature in the dark, the resin was filtered, washed as described above and dried in vacuo to give a light cream polymer.

Resin 2a-1.2: Elemental analysis calcd (%) for $(C_8H_8)_6(C_8H_7Br)$: C 83.53, H 6.89, Br 9.58; found: C 83.28, H 6.91, Br 9.79 corresponding to 1.2 mmol of Br per g of polymer; IR (CsI): $\tilde{\nu} = 1408$ (w), 1112 (w), 1011 (m; C–Br), 825 cm^{-1} (m); MS (EI, 408 °C): *m/z* (%): 169 (4) $[C_7H_6Br]$, 182 (7) $[C_8H_7Br]$, 249 (2) $[C_7H_5Br_2]$, 262 (4) $[C_8H_6Br_2]$.

Resin 2a-2.6: Elemental analysis calcd (%) for $(C_8H_8)_2(C_8H_7Br)$: C 73.66, H 5.92, Br 20.42; found: C 73.19, H 5.92, Br 20.72 corresponding to 2.6 mmol Br per g polymer; IR (CsI): $\tilde{\nu} = 1408$ (m), 1112 (w), 1011 (s; C–Br), 825 cm^{-1} (s); MS (EI, 408 °C): *m/z* (%): 169 (17) $[C_7H_6Br]$, 182 (33) $[C_8H_7Br]$, 249 (6) $[C_7H_5Br_2]$, 262 (16) $[C_8H_6Br_2]$, 340 (2) $[C_8H_5Br_3]$; DSC (peak maxima): 426 °C (endothermal; $\Delta H = -0.56\ kJ\,g^{-1}$); TG (weight loss): 71.5% (349 °C), 28.2% (551 °C), 0.3% residue.

Resin 2a-5.7: Elemental analysis calcd (%) for (C_8H_7Br): C 52.49, H 3.85, Br 43.66; found: C 50.20, H 3.85, Br 45.54 corresponding to 5.7 mmol Br per g polymer (this is more than that expected for mono-brominated rings and thus indicates further bromine incorporation either at the *ortho* or *meta* positions of the aromatic rings); IR (CsI): $\tilde{\nu} = 1409$, 1406 (m), 1025 (s; C–Br), 832, 828, 824 cm^{-1} (s); MS (EI, 408 °C): *m/z* (%): 103 (98), 104 (17), 169 (51) $[C_7H_6Br]$, 182 (100) $[C_8H_7Br]$, 249 (7) $[C_7H_5Br_2]$, 262 (22) $[C_8H_6Br_2]$.

Resin 2b-3.2: Elemental analysis calcd (%) for $(C_8H_8)_{16}(C_8H_7Br)_{13}$: C 68.87, H 5.46, Br 25.67; found: C 68.31, H 5.59, Br 25.89 corresponding to 3.2 mmol Br per g polymer; IR (CsI): $\tilde{\nu} = 1408$ (m), 1120 (w), 1014 (s; C–Br), 1011 (s), 825 cm^{-1} (s); MS (EI, 408 °C): *m/z* (%): 169 (15) $[C_7H_6Br]$, 182 (43) $[C_8H_7Br]$, 249 (1) $[C_7H_5Br_2]$, 262 (3) $[C_8H_6Br_2]$.

Lithiation and silylation of brominated polystyrene resins 2a and 2b: The brominated resin (1–5 g) was allowed to swell in benzene or toluene (20–60 mL) for 0.5 h. *n*BuLi (2.5 equiv, 2.6 M in toluene) was then added with a syringe and the resulting suspension was stirred at 60 °C. After the indicated times (60, 120 and 180 min), a few drops of the suspension were removed by pipette, quenched with MeOH, washed with MeOH (3 ×) and Et_2O (3 ×), dried in vacuo and analysed by IR spectroscopy and EI-MS.[13] After 3 h, the resin was filtered and washed twice with benzene or toluene.

Cl_2SiR_2 (R = Me, *i*Pr) (2.5 equiv based on starting bromine content) was added with a syringe to the lithiated resin, swollen in benzene or toluene. After the indicated times (30, 60 and 120 min), a few drops of the suspension were removed by pipette, quenched with H_2O in pyridine, washed with MeOH/H_2O, MeOH (2 ×) and Et_2O, dried in vacuo and analysed by IR spectroscopy and EI-MS.[13] After stirring for 2 h at room temperature, the resin was filtered, washed with THF (3 ×) and CH_2Cl_2 (3 ×) and dried in vacuo to give a yellow polymer.

Resin 3: IR (CsI): $\tilde{\nu} = 1399$ (w), 1383 (w), 1112 (m), 1001 (w), 883 (m), 823 cm^{-1} (m); MS (EI, 406 °C): *m/z* (%): 167 (11) $[C_8H_7SiCl+H]$, 181 (43) $[C_8H_7SiMeCl]$, 209 (31) $[C_8H_7Si(iPr)Cl]$, 252 (7) $[C_8H_7Si(iPr)_2Cl]$.

Resin 4: IR (CsI): $\tilde{\nu} = 1401$ (w), 1376 (w), 1115 (m), 840 (m), 813 (m), 789 cm^{-1} (m); MS (EI, 408 °C): *m/z* (%): 145 (9), 161 (14) $[C_8H_7SiMe_2]$, 181 (36) $[C_8H_7SiMeCl]$, 196 (10) $[C_8H_7SiMe_2Cl]$.

Attachment of 2,2′,6,2″-terpyridines to silylated polystyrene: 2,2′,6,2″-Terpyridine L^1OH or L^2OH (0.6–1.2 equiv based on starting bromine content) as a solid was added to the silylated resin (1–5 g) in CH_2Cl_2 (20–50 mL), and the suspension was stirred for 0.5 h. Diisopropylethylamine (1 mL per g of resin) and DMAP (10 mg per g of resin) were then added to the grey suspension. After the indicated times (60, 120, 240, 390 and 1440 min), a few drops of the suspension were removed by pipette, washed alternately with MeOH and DMF until the washings remained colourless upon treatment with a few drops of a Fe^{II} salt solution [$Fe(BF_4)_2$ in MeOH][14] and finally with CH_2Cl_2 (3 ×), dried in vacuo and analysed by IR spectroscopy and EI-MS.[13] After stirring for 24 h at room temperature, the resin was filtered, washed with CH_2Cl_2 and re-suspended in CH_2Cl_2. After the addition of MeOH (5 mL per g of resin) and diisopropylethylamine (1 mL per g of resin), the resin was stirred for 2 h at room temperature. Washing with MeOH, DMF and finally CH_2Cl_2 (3 ×) as described above and drying in vacuo yielded a yellow resin, which upon treatment with a few drops of a Fe^{II} salt solution in DMF turned purple[14] within a few seconds.

Resin 5-0.16 prepared from 2a-1.2: Elemental analysis calcd (%) for $(C_8H_8)_6(C_{35}H_{35}N_3OSi)_{0.14}(C_{15}H_{24}OSi)_{0.86}$: C 86.43, H 8.11, N 0.64; found: C 88.77, H 8.16, N 0.66 corresponding to 0.16 mmol of L^1 per g polymer; IR: $\int(1514\ cm^{-1})/\int(1494\ cm^{-1}) = 0.55$; MS (EI, 403 °C): *m/z* (%): 456 (2) $[C_8H_7Si - OL^1+H]$, 470 (8) $[C_8H_7SiMe - OL^1]$, 498 (16) $[C_8H_7Si(iPr) - OL^1]$, 541 (6) $[C_8H_7Si(iPr)_2 - OL^1]$.

Resin 5-0.23 prepared from 2a-2.6: Elemental analysis calcd (%) for $(C_8H_8)_2(C_{35}H_{35}N_3OSi)_{0.11}(C_{15}H_{24}OSi)_{0.89}$: C 81.55, H 8.49, N 0.95; found: C 83.65, H 7.85, N 0.95 corresponding to 0.23 mmol L^1 per g polymer; IR: $\int(1514\ cm^{-1})/\int(1494\ cm^{-1}) = 1.03$; MS (EI, 406 °C): *m/z* (%): 456 (6) $[C_8H_7Si - OL^1+H]$, 470 (17) $[C_8H_7SiMe - OL^1]$, 498 (38) $[C_8H_7Si(iPr) - OL^1]$, 541 (16) $[C_8H_7Si(iPr)_2 - OL^1]$; DSC (peak maxima): 433 °C (endothermal; $\Delta H = -0.46\ kJ\,g^{-1}$); TG (weight loss): 64.5% (362 °C), 29.5% (570 °C), 6.0% residue (probably SiO_2).

Resin 5-0.24 prepared from 2a-1.2: Elemental analysis calcd (%) for $(C_8H_8)_6(C_{35}H_{35}N_3OSi)_{0.23}(C_{15}H_{24}OSi)_{0.77}$: C 86.30, H 7.98, N 1.03; found: C 88.65, H 7.83, N 1.02 corresponding to 0.24 mmol L^1 per g polymer. IR: $\int(1514\ cm^{-1})/\int(1494\ cm^{-1}) = 0.88$; MS (EI, 408 °C): *m/z* (%): 456 (6) $[C_8H_7Si - OL^1+H]$, 470 (17) $[C_8H_7SiMe - OL^1]$, 498 (39) $[C_8H_7Si(iPr) - OL^1]$, 541 (15) $[C_8H_7Si(iPr)_2 - OL^1]$.

Resin 5-0.46 prepared from 2a-2.6: Elemental analysis calcd (%) for $(C_8H_8)_2(C_{35}H_{35}N_3OSi)_{0.25}(C_{15}H_{24}OSi)_{0.75}$: C 81.57, H 8.13, N 1.98; found: C 82.76, H 7.40, N 1.95 corresponding to 0.46 mmol L^1 per g polymer. IR: $\int(1514\ cm^{-1})/\int(1494\ cm^{-1}) = 2.10$; MS (EI, 407 °C): *m/z* (%): 104 (92), 456 (11 $[C_8H_7Si - OL^1+H]$, 470 (45) $[C_8H_7SiMe - OL^1]$, 498 (100) $[C_8H_7Si(iPr) - OL^1]$, 541 (42) $[C_8H_7Si(iPr)_2 - OL^1]$.

All resins 5: IR (CsI): $\tilde{\nu} = 1586$ (s), 1568 (m), 1514 (s), 1467 (m), 1390 (m; pyridine A_1 and B_1), 1268 (m, br), 884 (w), 823 (w), 793 cm^{-1} (m).

Resin 6 prepared from 2a-2.6: IR (CsI): $\tilde{\nu} = 1586$ (s), 1568 (m), 1514 (s), 1467 (m), 1390 (m; pyridine A_1 and B_1), 1267 (m, br), 884 (w), 823 (w), 793 cm^{-1} (m); MS (EI, 407 °C): *m/z* (%): 104 (94), 380 (2) $[C_8H_7Si - OL^2+H]$, 394 (3) $[C_8H_7SiMe - OL^2]$, 422 (100) $[C_8H_7Si(iPr) - OL^2]$, 465 (8) $[C_8H_7Si(iPr)_2 - OL^2]$.

Cleavage procedure: TBAF · 3 H_2O (3 equiv based on the starting terpyridine content) and acetic acid (3 equiv based on the starting terpyridine content) was added to the terpyridine resin swollen in THF (20–40 mL). The suspension was stirred at room temperature. After the indicated times (15, 30, 60, 120, 240 and 360 min), a few drops of the suspension were removed by pipette, washed alternately with MeOH and DMF, until the washings were colourless upon treatment with a few drops of a Fe^{II} solution,[14] and finally with CH_2Cl_2 (3 ×), dried in vacuo and analysed by IR spectroscopy and EI-MS.[13] Treatment of the final resin with Fe^{II} salts in DMF showed no colour change.

Resin 7 prepared from 5-0.46: IR (CsI): $\tilde{\nu} = 1400$ (w), 1365 (w), 1117 (m), 1001 (w), 884 (m), 825 cm^{-1} (m); MS (EI, 408 °C): *m/z* (%): 151 (6) $[C_8H_7SiF+H]$, 165 (30) $[C_8H_7SiMeF]$, 193 (21) $[C_8H_7Si(iPr)F]$, 217 (7) $[C_8H_7Si(iPr)_2]$, 236 (5) $[C_8H_7Si(iPr)_2F]$.

Resin 8 prepared from 5-0.24: IR (CsI): $\tilde{\nu} = 3645$ (m), 3480 (br) [OH], 1400 (w, sh), 1377 (br), 1115 (m), 1001 (w), 909 (m), 883 (m), 825 (w, sh),

820 cm^{-1} (w; Si–OH); MS (EI, 408 °C): *m*/*z* (%): 149 (14) [$C_8H_7SiOH+H$], 163 (59) [$C_8H_7SiMeOH$], 191 (50) [$C_8H_7Si(iPr)OH$], 234 (6) [$C_8H_7Si(iPr)_2OH$].

Acknowledgements

We gratefully acknowledge the permanent, generous support from Prof. Dr. G. Huttner.

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[13] The time for drying of resins (usually 24 – 48 h) can be reduced for fast MS reaction control to about 15 – 30 min under reduced pressure as the adsorbed solvent is then removed in the MS spectrometer at temperatures below 200 °C, so that solvent molecules do not interfere with the resin measurement at $T > 400$ °C.

[14] The typical colour of terpyridine – Fe^{II} complexes is purple; see, for example: a) F. Lions, I. G. Dance, J. Lewis, *J. Chem. Soc. A* **1967**, 565 – 572; b) J. S. Judge, W. M. Reiff, G. M. Intille, P. Ballway, W. A. Baker, Jr., *J. Inorg. Nucl. Chem.* **1967**, *29*, 1711 – 1716; c) R. Hogg, R. G. Wilkins, *J. Chem. Soc.* **1962**, 341 – 350.

Received: April 20, 2000 [F2438]

  0947-6539/00/0622-4210 $ 17.50+.50/0