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Structure, Mobility, and Domain Sizes in Poly(chloromethylsilane-*co*-styrene)

E. Brendler,*,[†] Ch. Jäger,[§] D. Scheller,[⊥] and G. Roewer[‡]

Institut für Analytische Chemie and Institut für Anorganische Chemie,
Technische Universität Bergakademie Freiberg, Leipziger Strasse 29, 09596 Freiberg, Germany;
Institut für Optik und Quantenelektronik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1,
07743 Jena, Germany; and Institut für Organische Chemie, Technische Universität Dresden,
Mommsenstrasse13, 01062 Dresden, Germany

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ABSTRACT: The structure of poly(chloromethylsilane-*co*-styrene) obtained from styrene and chloromethyldisilanes is investigated by HR liquid and solid-state NMR techniques. $^{1}H-^{13}C$ DEPT and $^{1}H-^{29}Si$ HMBC investigations indicate that the system has to be considered as a polymer blend consisting of poly(chloromethylsilane) and polystyrene. Differences in the mobility of the two polymers are demonstrated by $^{1}H-^{13}C$ WISE spectroscopy. The results of spin diffusion investigations carried out on poly(chloromethylsilane-*co*-styrene) samples indicate surprisingly small polystyrene domains.

Introduction

Organosilicon polymers with a wide variety of architectures and reactivities present a large base of substances for SiC preceramic polymers. Recently a novel reaction route has been reviewed[1] involving a heterogeneous Lewis-base-catalyzed disproportionation of chloromethyldisilanes obtained from the Müller−Rochow synthesis. The resulting organosilicon polymers can be spun into poly(chloromethylsilane) fibers by a melt-spinning process.[2] Styrene was polymerized together with the chloromethyldisilanes to improve the rheologic behavior for spinning and stretching of the polysilane fiber. The question of whether the styrene is distributed in the resulting organosilicon polymer statistically or not was investigated earlier by ^{13}C NMR spectroscopy.[3] Signals characteristic of polystyrene were observed. They are indicating that either a copolymer with large polystyrene and poly(chloromethylsilane) blocks or a polymer blend has been formed. The investigations presented in this paper will give an answer to this remaining question and the problem of how large the obtained domains are. Solution and solid-state NMR spectroscopic methods such as spectral editing with DEPT, $^{1}H-^{29}Si$ heteronuclear multiple bond correlation (HMBC), $^{1}H-^{13}C$ wide-line separation spectroscopy (WISE), and spin diffusion investigations were used to gather the desired information.

Experimental Section

Poly(chloromethylsilane-*co*-styrene) samples were prepared according to ref 1. The polymers investigated here contained about 70% poly(chloromethylsilane) and 30% polystyrene. For NMR measurements in solution the polymers were dissolved under argon in dry deuteriochloroform.

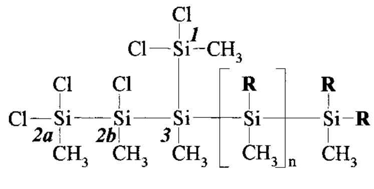
^{1}H, ^{13}C, and ^{29}Si HR NMR investigations were carried out at a Bruker DPX 400 (10 mm multinuclear probehead) and a DRX 500 (HMBC and HSQC: 5 mm multinuclear inverse probehead with *z*-gradient).

Solid-state MAS NMR investigations were carried out at a Bruker MSL 300 and an AMX 400 spectrometer (spin diffusion) using 7 mm zirconia rotors and a 7 mm standard CP-MAS probehead. If not specified otherwise, a spinning speed of 5 kHz was applied to avoid the superposition of spinning sidebands and isotrope signals. CP contact times were either 50 μs (spin diffusion measurements) or 5 ms. The rotors were filled in a glovebox to keep the samples free of moisture and oxygen.

Results and Discussion

Two major problems had to be investigated: (i) whether the two polymers polystyrene and poly(chloromethylsilane) form a block copolymer or a polymer blend and (ii) to get an estimation of the PS domain sizes obtained by this polymerization route.

(i) Poly(chloromethylsilane-*co*-styrene) (PSCS) can be synthesized either by reacting a mixture of 1,1,2,2-tetrachlorodimethyldisilane (TCDMDS) and styrene in the presence of a Lewis base catalyst[1,3−5,12] or by heating poly(chloromethylsilane) (PCMS) obtained from TCDMDS together with styrene.[15] ^{29}Si and ^{13}C NMR spectra of the products of both reactions indicated that PCMS and polystyrene (PS) were formed. Figure 1 shows the ^{13}C CP-MAS spectrum of a representative PSCS sample. The three upfield signals arise from the methyl groups bound to the silicon backbone of the PCMS polymer, the structure of which can be described by the general formula with R = Cl, $SiCH_3R_2$:



Previous investigations[6] showed that it can be distinguished between CH_3Cl_2Si- end groups [***1***] bound to silicon branching units, short linear units $CH_3Cl_2Si-SiCH_3Cl-$ and $-SiCH_3Cl-$ spacers [***2a,b***], and branching units $\equiv SiCH_3$ [***3***]. As far as branching units are

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[†] Institut für Analytische Chemie, Technische Universität Bergakademie Freiberg.
[‡] Institut für anorganische Chemie, Technische Universität Bergakademie Freiberg.
[§] Friedrich-Schiller-Universität Jena.
[⊥] Technische Universität Dresden.

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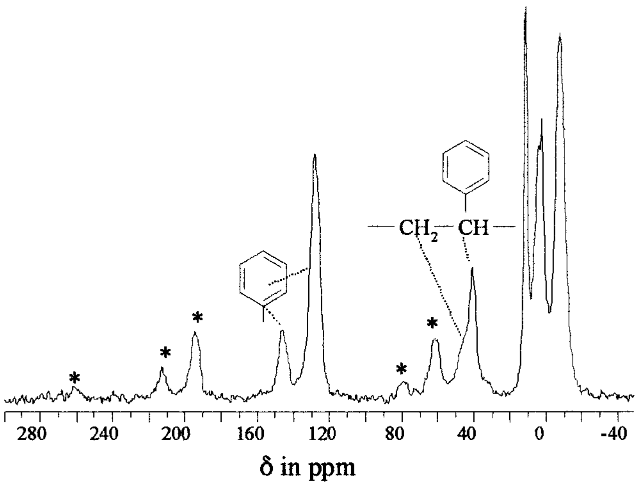
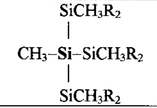


Figure 1. ^{13}C CP-MAS spectrum of a poly(chloromethylsilane-*co*-styrene) sample. Resonance frequency 75.47 MHz, spinning speed $\nu_R = 5$ kHz, CP contact time 5 ms.

Table 1. Structure Groups and Chemical Shifts of Poly(chloromethylsilane)[a]

No.	structure elements	chemical shifts / ppm		
		^1H	^{13}C	^{29}Si
1	Cl_2CH_3Si– attached to 3	1.05	11	36.7
2 a	Cl_2CH_3Si– attached to 2b	0.9	2	25.8
2 b	–$SiCH_3Cl$– spacer			14.2
3	 $CH_3{-}\underset{SiCH_3R_2}{\overset{SiCH_3R_2}{Si}}{-}SiCH_3R_2$	-0.4	-7.7	-63

[a] The ^{13}C and ^{29}Si chemical shifts vary within 0.5 ppm depending on the composition and cross-linking density of the samples.

concerned, silicon is bound to three other silicon units forming the three-dimensional polymer network. Table 1 gives the chemical shifts of all groups. The signals have been advised to the different structure groups using the chemical shifts of intermediate and related oligosilanes[6,17] and by deconvolution of the polymer spectra on the basis of IRCP (inversion recovery cross-polarization) investigations.[1]

The structure is dominated by the branching units, leading to cyclic and cagelike structures. The cross-linking density of the PCMS polymer is about 2. The assignments for the PS signals are also given in Figure 1. The chemical shifts are identical with those of the pure PS and PCMS polymers. This result indicates the formation of PCMS and PS blocks. A statistical distribution of the starting comonomers is not achieved in the final polymer.[3]

Two facts gave rise to the assumption that the polymer blocks could be connected by $-SiCH_3R-CH_2-CHPh-$ links. First, the intensity of the signal for the CH_3Cl_2Si- end groups decreased slightly in comparison with the pure PCMS polymer. Second, as can be seen from Figure 2, methylene signals at about 15, 18, and 34 ppm could be detected by DEPT spectroscopy with an intensity of up to 5%. These chemical shifts are typical for methylene groups bound to silicon.[7]

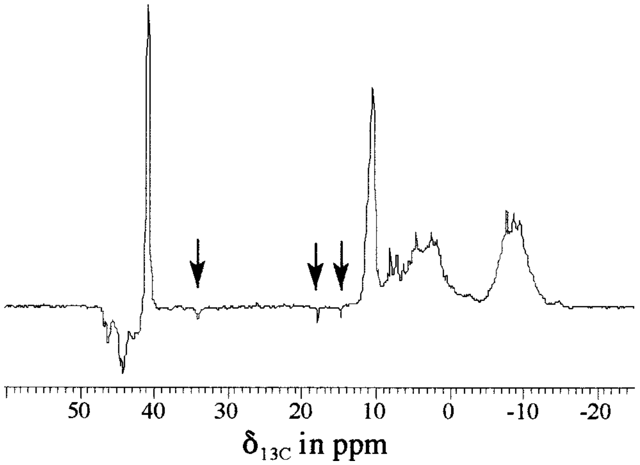


Figure 2. Upfield part of the ^{13}C DEPT-135 spectrum of a poly(chloromethylsilane-*co*-styrene) sample dissolved in $CDCl_3$. Resonance frequency 100.13 MHz. The arrows indicate the methylene groups shifted upfield.

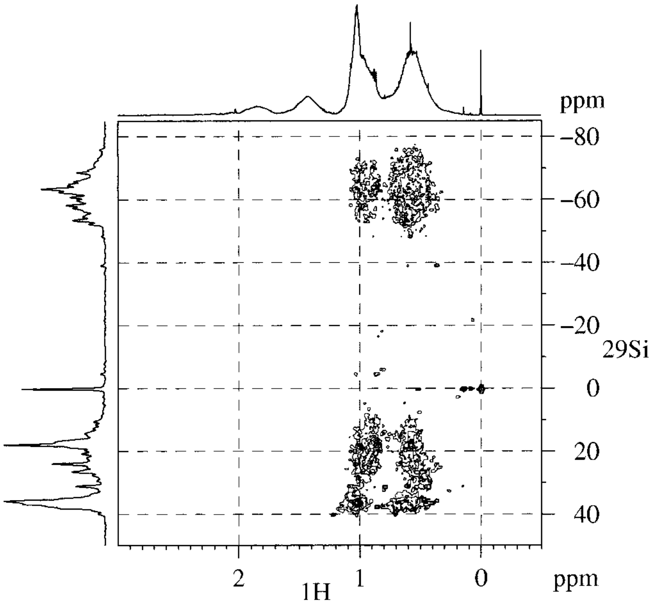


Figure 3. $^1H-^{29}Si$ HMBC spectrum of a PSCS sample. Resonance frequency 500 MHz (^1H), 99.45 MHz (^{29}Si), experiment time 13 h. The signal at 0 ppm in both dimensions arises from $(CH_3)_4Si$. The ^1H NMR spectrum displayed at the axis is not the projection but was recorded in a separate 1D experiment.

$^1H-^{29}Si$ HMBC spectroscopy of the dissolved polymer sample was applied to search for connectivities between PS and PCMS. The spectrum obtained is shown in Figure 3. The ^1H and ^{29}Si NMR chemical shifts and the underlying structure groups are listed in Table 1. The ^1H NMR signals between 1.2 and 2 ppm arise from polystyrene protons bound to the aliphatic carbons of the polymer. Besides the strong correlation signals between the protons of methyl groups and the silicon atoms of the PCMS network (for δ_{Si}(36.7 ppm): signal/noise = 720) no other cross-peaks are detected. Therefore, we conclude that both polymers are not connected by chemical bonds to a significant amount in the sense of NMR spectroscopy. Thus, the system is considered to be a polymer blend.

Two other observations substantiate this conclusion. GPC investigations result in a bimodal molecular weight distribution for PSCS polymers.[12] Furthermore, a slight but significant separation of PS and PCMS during melt-spinning of polymers containing more than 30% PS could be observed by ^{13}C CP-MAS NMR.[16] The decrease

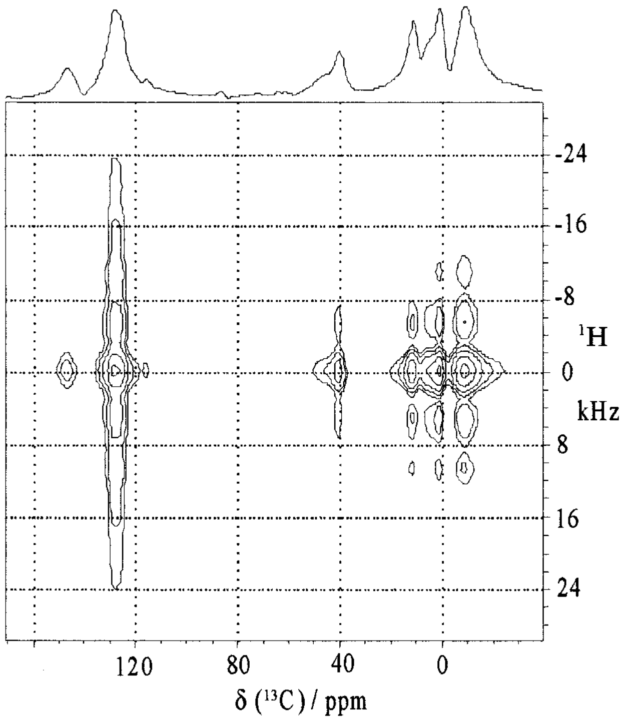


Figure 4. $^1H-^{13}C$ WISE spectrum of a PSCS sample. $\nu_R = 4$ kHz. A TOSS sequence was applied to eliminate spinning sidebands in the ^{13}C dimension. Note that the PCMS signals and the PS signal at 128 ppm have the same intensity.

in the concentration of the CH_3Cl_2Si- end groups was obviously due to the different reaction times for the PSCS polymer in comparison with the pure PCMS. This results in a higher cross-linking density within the poly(chloromethylsilane) part of the PSCS polymer. A beginning carbosilane formation can be another explanation for the weak CH_2 signals between 15 and 20 ppm in the ^{13}C spectra. Chemical shifts of about 15 ppm have also been reported for methylene groups in small, isolated styrene units.[13,14] $^1H-^{13}C$ HSQC (heteronuclear single quantum coherence) spectra showed that the protons responsible for the signal at 34 ppm are not equivalent. This can be explained by the appearance of small oligomeric styrene units having different R_1 and R_2 for the methylene groups $R_1-CH_2-R_2$.

(ii) Investigation of Domain Sizes. The determination of domain sizes for block copolymers and polymer blends by spin diffusion measurements has been studied extensively by Schmidt-Rohr and co-workers.[8,10] In principle the ^1H magnetization of one polymer is selected, and their spin diffusion behavior is studied using ^{13}C detection. The proton magnetization equilibration rate of the whole polymer is determined by the spin diffusion constant as well as by the size and the shape of the polymer blocks. The selection of the proton magnetization can be achieved either by a chemical shift filter, if the resonance frequencies of the polymers can be resolved by CRAMPS, or by a dipolar filter for blends having different dynamics in the two polymer phases. ^1H MAS spectra and $^1H-^{13}C$ WISE spectra of the polymers investigated here show a different mobility for the two components with, as expected from literature,[9] relatively rigid PS and more mobile CH_3 groups of the silicon polymer. Figure 4 shows a $^1H-^{13}C$ WISE spectrum of a PSCS sample.

The higher mobility of the protons in the PCMS region is indicated by the smaller line width in the ^1H dimension. For that reason the dipolar filter was chosen to select the ^1H magnetization of the PCMS region for spin diffusion investigations. Figure 5 shows the pulse sequence used. Unfortunately the system has very short T_2 relaxation times in comparison with the samples used to develop and to demonstrate the methods.[8,10] For that reason only two cycles of the dipolar filter could be applied. Sideband suppression (TOSS sequence) had been omitted to avoid any additional loss of signal intensity. The resulting spectra are shown in Figure 6a; Figure 6b gives the corresponding integrals for the PS signals.

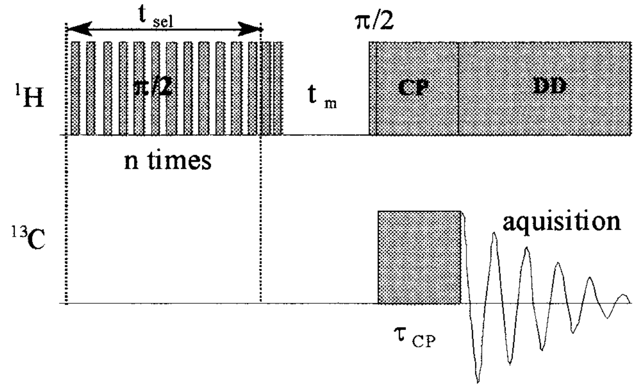


Figure 5. Pulse sequence for the spin diffusion experiments on PSCS, $n = 2$, delay between the filter pulses: 8 μs. The dipolar filter is followed by two $\pi/2$ pulses to eliminate T_1 effects. No TOSS sequence was applied to avoid any unnecessary loss of signal intensity.

In comparison with the investigations and calculations carried out for other PS-containing systems,[10] the magnetization is equilibrating much faster than expected for a polymer blend. It is comparable to the behavior in copolymers with domain sizes of only about 2−5 nm, leading to the conclusion that the PS domains are very small.

The intensity changes observed in the poly(chloromethylsilane) part of the spectrum were due to the effect of the dipolar filter in the PCMS itself. As expected from the polymer structure, the mobility of the methyl groups is larger for the CH_3Cl_2Si- end groups than for the backbone of the polymer. Therefore, a loss of intensity for the latter signals was observed in the filtered spectrum. The intensity of these signals recovered during the experiment and was consistent with the ^{13}C CP-MAS spectrum for a contact time of 50 μs after a spin diffusion time of about 500 μs.

Summary and Outlook

Poly(chloromethylsilane-*co*-styrene) polymers obtained by the reaction of methylchlorodisilanes and styrene can be considered as polymer blends. The polystyrene domains are surprisingly small. Such small PS domains could possibly arise from a PS film covering the PCMS areas, which may also explain the good material properties of the silicon carbide fibers spun and pyrolyzed from PCS. Although the PS decomposes, the compact structure of the fibers remains intact, as demonstrated in ref 1.

It was possible to investigate several polymer samples, but the applicability of the dipolar filter for selecting the ^1H magnetization of the mobile polymer component is limited by the short T_2 relaxation times of the samples and the small mobility differences for the different proton environments.

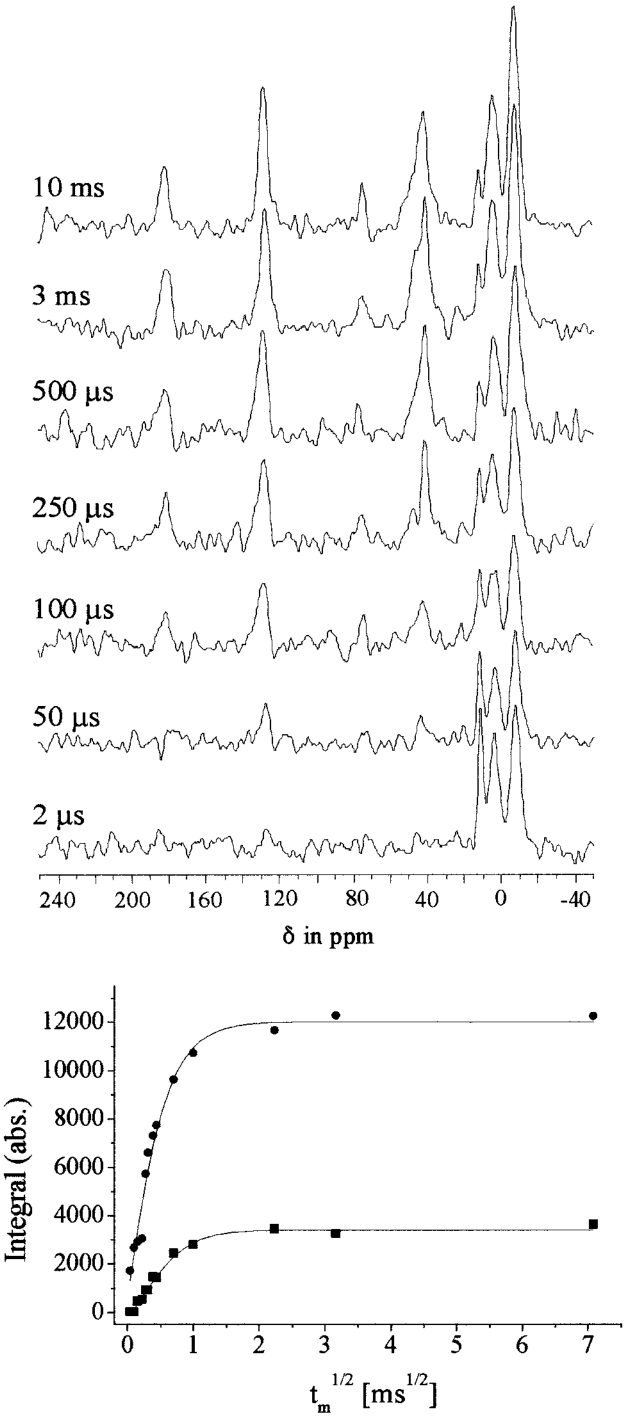


Figure 6. (a) ^{13}C CP-MAS spectra with ^{1}H dipolar filter, mixing time (see spectra) for spin diffusion and CP to ^{13}C, $n = 2$, resonance frequency 75.47 MHz, $\nu_R = 4$ kHz. (b) Dependence of the integral of the phenyl (●) and −CH− (■) groups of polystyrene on the mixing time.

In addition, we observed that the efficiency of the dipolar filter decreases very fast with the age of the sample. Cross-linking between the poly(chloromethylsilane) units due to moisture in an amount hardly detectable by chemical analysis or NMR leads to a rapid mobility loss for the methyl protons of the PCMS regions. Therefore, it will be interesting to investigate whether a chemical shift filter using CRAMPS to select for example the polystyrene component as a source of magnetization is practicable in this system. This would give the possibility to investigate polymers obtained by other reaction schemes and over a wider range of poly(chloromethylsilane)/polystyrene ratios.

In combination with the characterization of the SiC materials obtained after curing and pyrolysis of the polymer, the determination of the structure, mobility, and domain sizes in this polymer blend system gives a unique chance to relate the structural characteristics of polymer precursors to the properties of the resulting materials.

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