Structure of a PDMS Layer Grafted onto a Silica Surface Studied by Means of DSC and Solid-State NMR

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Received November 2, 2001

ABSTRACT: The structure of a poly(dimethylsiloxane) (PDMS) layer at the surface of hydrophilic silica has been studied by means of DSC, proton NMR T_2 relaxation experiments, and ^{1}H and ^{29}Si NMR spectroscopy. The samples were prepared using (1) the adsorption of PDMS from a PDMS solution onto the silica surface followed by a thermal treatment and (2) mechanical mixing of PDMS with the silica followed by the separation of bound rubber. It was shown that these procedures caused the formation of chain loops chemically attached to the silica surface at both chain ends. The average length of the grafted chains varied from about four to eight Si−O bonds. The experiments provided information on the mobility of the grafted chains, which is related to the structure of the grafted layer. The grafted PDMS layer was found to consist of immobilized chain segments at the PDMS−silica interface and mobile chain portions outside the interface. The chain immobilization at the interface caused a substantial decrease in the heat capacity at T_g and suppressed crystallinity of the grafted PDMS. The interface fraction increased proportionally with a decreasing chain length. About four dimethylsiloxane pendant chain units next to the grafting site were immobilized due to chain anchoring to the silica surface. A small fraction of $-SiO(CH_3)_2-$ chain units was immobilized as a result of physical adsorption at the silica surface. The fraction of physically adsorbed chain units appears to be proportional to the number of residual silanol groups at the silica surface. The mobility of the chain portions outside the interface was found to differ significantly in the various samples studied and to increase with an increasing average length of the grafted chains. The NMR method allowed us to make a distinction between a dense "brushlike" structure of the grafted layer containing grafted chains of a fairly uniform length and a layer containing a significant fraction of long chain loops outside the densely grafted layer. It was found that the structure of the grafted layer is to a great extent dependent on the grafting procedure employed.

Introduction

Chain grafting is widely used to improve the miscibility of components in polymer mixtures and blends. Understanding the effect of chain grafting on the structure of the interfacial layer is of importance in many polymeric applications. Polymer brushes, densely grafted polymers chains, are the systems that have been studied the most both experimentally and theoretically.[1−12] The majority of the polymer brush studies carried so far have focused on long chains grafted to the surface of solids at their ends. Several structural characteristics of the grafted layers have been analyzed, i.e., the average thickness of the grafted layer, the monomer density profiles, the distribution of chain ends, and the effect of solvents and the geometry of the solid surface on the aforementioned characteristics. Less information is available on short grafted polymeric chains. The studies focusing on these issues have concentrated mainly on modified types of porous silica used as supports in high-performance liquid chromatography or as solid-supported catalysts.[13−16]

Fumed silicas find wide application in the reinforcement of silicon rubbers and the thickening of polymeric liquids. Grafting polymer chains onto the surface of fumed silicas allows modification of silica−silica and silica−polymer interactions.[17] Variations in the grafting density, its heterogeneity, and the average length of the grafted chains have a significant effect on silica−silica interactions and interactions of silica particles with the matrix material. It follows that knowledge of the molecular structure of the grafted layer is needed for a complete understanding of the molecular mechanisms responsible for the reinforcing and thickening effects. Solid-state NMR spectroscopy and NMR relaxation studies are among the most informative methods to obtain information on the chemistry of grafting, chain order, chain conformation, and molecular mobility of short grafted chains.[10−16,18,19]

The molecular mobility of high-molecular-mass poly(dimethylsiloxane) (PDMS) chains grafted at one end and of PDMS that is physically adsorbed at the silica surface has previously been studied with the aid of various solid-state NMR techniques.[10−12,18,19] It was found that long PDMS chains, which are chemically attached to the silica surface, undergo uniaxial reorientations around the direction normal to the solid−polymer interface.[10−12] Physically adsorbed PDMS chains form an immobilized layer at the silica surface.[18,19] These studies showed that NMR relaxation methods are highly sensitive to heterogeneous mobility of PDMS chains at a silica surface. Since molecular mobility is closely coupled to chain length, grafting density, and chain length distribution, NMR relaxation methods can provide valuable information on the structure of grafted layers.

The present study focuses on the structure of PDMS layers on the surface of fumed silicas. Two different methods were used for sample preparation. One method was based on the adsorption of PDMS from a PDMS solution onto the silica surface followed by a thermal

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10.1021/ma0119124 CCC: $22.00

Table 1. Structural Characteristics of Silylated Silicas

sample	1A	2A	2B	2C	2D
preparation method	1	2	2	2	2
reaction temp, °C	300	150	100	150	50
reaction time, h	4	0.5	2	0.5	2
carbon content, wt %	9.62	10.25	14.2	11.4	8.6
PDMS content, wt %[a]	29.7	31.6	44.0	35.2	26.5
residual SiOH, %[b]	5.0	14.2	12.7	12.3	10.0
average chain length, N_t[c]	4.2	5.5	7.7	6.2	4.5

[a] Based on the carbon content. [b] With respect to the SiOH content of an initial hydrophilic silica, which is about 1.76 SiOH per 1 nm^2. [c] The average number of siloxane bonds, N_t, per grafted site was inferred from the PDMS content and the number of reacted SiOH groups. The N_t value corresponds to the total length of the chains grafted at one end, if present, and the half-length of chain loops and chains attached to neighboring silica particles.

treatment. The other method was based on mechanical mixing of PDMS with silica followed by the separation of bound rubber. The effects of the amount of PDMS on the silica surface and specific preparation method on the structure of the PDMS layer have been analyzed. Several techniques were used in this study: (1) DSC experiments provided information on glass transition and crystallinity, (2) ^{1}H and ^{29}Si NMR spectroscopy were used to analyze the chemical structure of the samples, and (3) low-resolution ^{1}H T_2 relaxation experiments were performed to analyze the PDMS−silica interface, chain length distribution of PDMS loops at the silica surface, and the effect of physical adsorption on the immobilization of PDMS at the silica surface.

Experimental Section

A. Samples Studied. 1. Preparation of Silylated Silicas. Surface modification was applied to hydrophilic fumed silica with a BET surface area of 300 m^2/g. Controlled surface coverage was realized using two different techniques.

Method 1 is based on the adsorption of PDMS from a PDMS solution onto the silica surface followed by a thermal treatment. An aerosol of 10 wt % PDMS solution in tetrahydrofuran (THF) was added to the silica fluidized by mechanical stirring. For this method, trimethylsiloxy-end-capped PDMS fluid with the gross formula $(CH_3)_3SiO[(CH_3)_2SiO]_{1050}Si(CH_3)_3$ was used. The viscosity of the PDMS fluid was 100 Pa·s at 25 °C. Several cycles of aerosol addition and subsequent drying of the mixture from THF were performed. The drying was effected at 120 °C under a stream of nitrogen. The PDMS content after the last cycle was about 30 wt %. The silica particles coated with the PDMS layer were subsequently heated at 300 °C for 4 h.

Method 2 is based on mechanical mixing of PDMS with silica, followed by the separation of bound rubber. The conditions were similar to those employed during the processing of a mixture of high-temperature-curing silicon rubbers. The initial mixture consisted of 60 wt % trimethylsiloxy-end-capped PDMS rubber, 10 wt % OH-terminated PDMS fluid and 30 wt % silica. The PDMS rubber and the fluid had the gross formulas $(CH_3)_3SiO[(CH_3)_2SiO]_{4700}Si(CH_3)_3$ and $HO[(CH_3)_2SiO]_{15}H$, respectively. Their viscosities at 25 °C were 10^4 and 0.025 Pa·s, respectively. The mixture was kneaded for 0.5−2 h at temperatures ranging from 50 to 150 °C (see Table 1). The rubbers were stored for approximately 2 months. Afterward, the mixtures were dispersed in THF for 48 h using a magnetic stirrer. The dispersion was then kept without stirring for 24 h, which resulted in sedimentation of silica aggregates coated with a PDMS layer. The supernatant, consisting of PDMS solution and a small amount of silica particles, was removed by means of decantation. A fresh portion of THF was added a few times followed by stirring and decantation until the concentration of PDMS in the supernatant THF solution was below 1 wt %. The total amount of silica in the PDMS/silica mixture (bound rubber) obtained was more than 90%, relative to the concentration in the initial mixture.

The following experiments were performed to characterize silylated silicas (see Table 1).

(1) The concentration of PDMS grafted onto the silica surface was inferred from the carbon content (% C) by determining the CO_2 content of combustion products using IR spectroscopy.

(2) The degree of silylation of the silica surface was determined by calculating the ratio (in % SiOH) of the amounts of silanol groups at the silica surface after and before silylation.

(3) The amount of silanol groups was measured by means of an acid−base titration using a solution of NaOH in a water/methanol mixture (50:50 wt %/wt %), following a procedure described by Sears.[20] It should be noted that only silanol groups on the silica surface are measured with this method.

(4)The *average number* of siloxane bonds, N_t, in the grafted chains was determined from the PDMS content and the number of reacted SiOH groups. A value of N_t corresponds to *the total length of chains anchored at one end, if present, and the half-length of chain loops and chains attached to neighboring silica particles*. Structural characteristics of silylated silicas are presented in Table 1.

2. Sample Preparation for NMR Experiments. About 0.37 g of each sample was placed into an 18 mm-diameter NMR tube with a length of 180 mm. The NMR experiments were performed using (a) *the samples as a whole*, (b) *the samples swollen in C_2Cl_4* and (c) *the samples swollen in C_2Cl_4 in an ammonia atmosphere*. Swollen samples formed turbid gels or suspensions. The volume fraction of PDMS, V_p, in swollen samples was 5.15 vol %. The V_p value was calculated using the specific densities of PDMS of 0.98 g/cm^3 and C_2Cl_4 of 1.623 g/cm^3. The volume fraction of SiO_2 was subtracted to determine the V_p value. To prevent evaporation of the solvent, a Teflon plug was inserted so that the bottom was just above the sample. The swollen samples were stored for 1 day before the experiments. Swelling in the presence of ammonia was performed in uncovered NMR tubes containing swollen samples. The tubes were placed in a flask containing a 25 wt % ammonia solution in water. The flask was then sealed with a stopper and the samples were stored under ammonia for 1 day prior to the experiments.

B. DSC. The DSC experiments were performed using a Perkin-Elmer Pyris-1 equipped with a cryofill. The purge gas was a mixture of 10% helium and 90% neon at a flow rate of 25 mL/min. The sample pans, which were supplied by v.d. Boel Eng. NL, had a volume of 40 μL. The temperature calibration of the analyzer was performed with the aid of adamantane, water, indium, and lead. The sample weight was in the range 10−20 mg. The samples were kept for 20 min at −150 °C before being heated at a rate of 20 °C/min.

C. The Solid-State NMR Experiments and Data Analysis. 1. Equipment. The proton NMR T_2 relaxation experiments were performed using a Bruker Minispec PC-120 spectrometer. This spectrometer operates at a proton resonance frequency of 20 MHz. The lengths of the 90 and 180° pulses and the dead time were 2.5 μs, 5.2 μs and 10 μs, respectively. The T_2 relaxation experiments were performed at 40 °C.

^{1}H MAS and ^{29}Si MAS NMR spectra were recorded with the aid of a Varian Inova-400 MHz wide-bore NMR spectrometer operating at a ^{1}H and ^{29}Si frequency of 400 and 79.5 MHz, respectively, using a 7 mm CP/MAS probe. The ^{1}H and ^{29}Si 90° pulse widths were 1.5 and 5 μs, respectively. All the spectra were recorded at room temperature.

2. The ^{1}H NMR T_2 Relaxation Experiments and Data Analysis. 2.1. T_2 Relaxation Experiments. Two different pulse sequences were used to record the decay of the transverse magnetization (T_2 decay) from both (semi)rigid and mobile fractions of the samples as previously described.[21] *The solid-echo pulse sequence* (SEPS), $90^\circ_x - t_{se} - 90^\circ_y - t_{se} -$ [acquisition: A[$f(t)$]], with $t_{se} = 20$ μs was used to determine the T_2 relaxation time and the proton content of the (semi)rigid fraction of the samples. The time after the first pulse $t = (2t_{se} + t_{90}/2)$ was taken to be zero, with t_{90} being the duration of the 90° pulse. *The Hahn-echo pulse sequence* (HEPS), $90^\circ_x - t_{He} - 180^\circ_x - t_{He} -$ [acquisition], was used to record the slow decay of the mobile fraction of the samples. The second pulse in the HEPS inverts nuclear spins of mobile molecules only and an echo signal is formed with a maximum at time $t = (2t_{He} + t_{180}/2)$ after the first pulse, where t_{180} is the duration of 180° pulse. By varying the pulse spacing t_{He} in the HEPS from 0.035 to 67.5 ms, the amplitude of the transverse magnetization, A(t), is measured as a function of time t. The HEPS makes it possible to eliminate magnetic field and chemical shift inhomogeneities, and to accurately measure the T_2 relaxation time of mobile materials. The analysis of data points measured separately by the SEPS and the HEPS showed that in the time interval ranging from 0.07 to 0.14 ms both experiments yielded similar values for the amplitude of the transverse magnetization. The total decay of the transverse magnetization was then reconstructed by combining the SEPS data in the time domain ranging from 0 to 0.14 ms with the HEPS data in the time interval from 0.07 to 135 ms.

The time constants (T_2 relaxation time), which are characteristic for different slopes in the magnetization decay curve, were obtained by performing a least-squares fit of the T_2 decay using a linear combination of two or three exponential functions. The results obtained with these functions were statistically relevant, unlike those obtained with several other functions used. *The relative fraction of the relaxation components*, designated in the text by $\%T_2^{index}$, represents the fraction of hydrogen in chain portions with different molecular mobilities that are responsible for the relaxation components.

The error in the relaxation parameters consisted of (a) experimental errors (about 2%), (b) an error ascribable to the chosen fitting function (estimated to be about 5%), and (c) uncertainties of the fitting (about 0.5%). Repeated experiments using the same sample showed that the standard deviation of the results was smaller than 2−3%.

3. ^{1}H and ^{29}Si NMR Spectroscopy. All the ^{1}H and ^{29}Si spectra were recorded using magic-angle spinning (MAS) with a MAS frequency of 7.6 kHz. Additionally, high-power proton decoupling was used to record the ^{29}Si spectra. The ^{29}Si spectra were referenced to the trimethylsilyl resonance of the cubic octamer silicic acid trimethylsilyl ester (Q_8M_8) observed at 11.7 ppm relative to tetramethylsilane (TMS). ^{1}H resonances were referred to TMS. Recycle delay times of 4 and 60 s were used in the ^{1}H and ^{29}Si experiments, respectively. A total of 1000 scans were accumulated for each spectrum.

Results and Discussion

1. Glass Temperature and Crystallinity As Determined by Means of DSC. DSC yields information on overall chain immobilization via the glass transition temperature, T_g, and a step in the heat capacity at T_g (ΔC_p). It is well-known that PDMS shows a glass transition at about −123 °C and at higher temperatures phase transitions caused by crystallization and melting. The thermal behavior of PDMS is compared with that of silylated silicas in Figure 1. All the silica samples showed a minor glass transition from about −118 to −123 °C. PDMS chains grafted onto a silica surface showed 13 to 50 times smaller ΔC_p compared to that of pure PDMS (see Table 2). This suggests substantial immobilization of a large fraction of the PDMS chains at the silica surface. It was thought that a gradual change in ΔC_p above −60 °C could be related to a second glass transition of the PDMS−silica interface. It will be shown below that an immobilized PDMS layer formed at the silica surface and that chain mobility in this layer was strongly constrained.

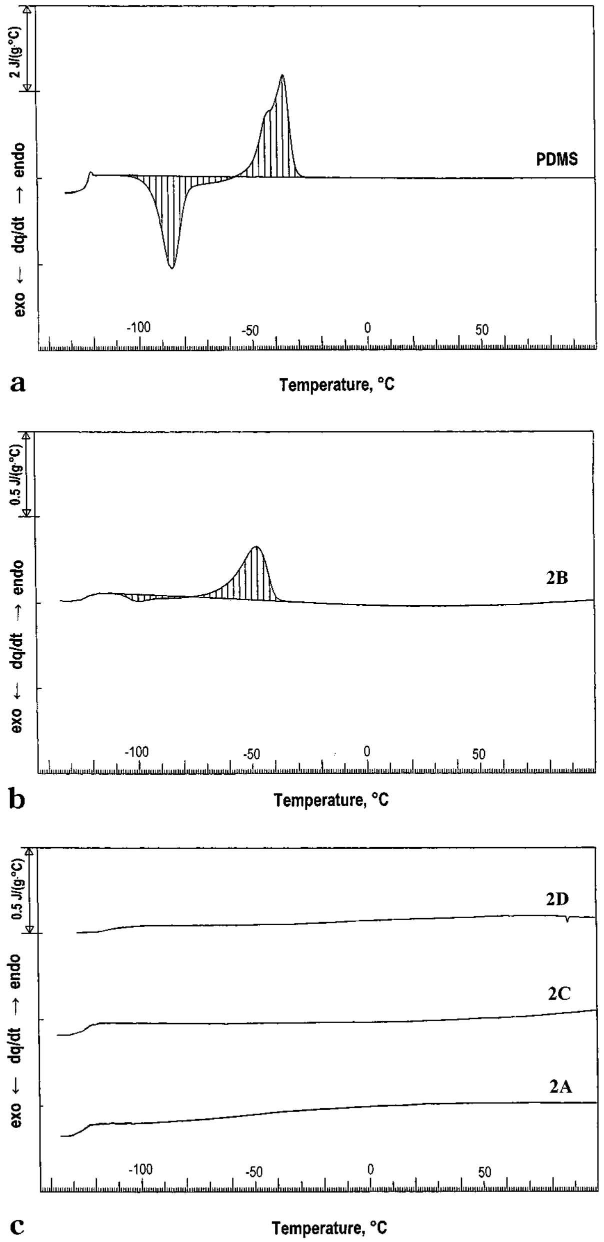


Figure 1. DSC continuous specific heat capacity curves of pure PDMS (a) and silylated silica 2B (b) and 2A, 2C, and 2D (c).

Table 2. The Thermal Behavior of Pure PDMS and Silylated Silicas

sample	T_g, °C^a	ΔC_p, J/(g·°C)^b	ΔC_p, J/(g·°C)^c	T_m, °C	ΔH_m, J/g^b	ΔH_m, J/g^c
PDMS	−123	0.40	0.40	−36	27.2	27.2
2A	−123	0.03	0.0095			
2B	−121	0.07	0.031	−48	5.4	2.4
2C	−123	0.05	0.018			
2D	−118	0.03	0.0080			

[a] Temperature of 50% increase in ΔC_p. [b] Per gram of the samples. [c] Per gram of PDMS.

Pure PDMS reveals an exothermic peak of cold crystallization at −85 °C and a melting endotherm with a maximum at −36 °C. The crystallization behavior of PDMS chains at the silica surface is related to topological constrains due to chain anchoring to the silica surface, which hamper crystallization. The only silylated silica that showed crystallinity in our examples is sample 2B. In the series of studied samples the amount of PDMS in silica was largest in 2B. The heat of melting of this sample was about 10 times smaller than that of pure PDMS. This means that just a small fraction of PDMS chain units in this sample could form a crystalline phase. Apparently, only fairly long PDMS chains, which are virtually not constrained by chain anchoring,

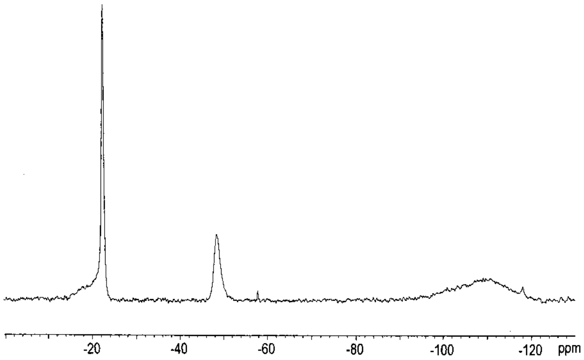


Figure 2. ^{29}Si NMR MAS spectrum obtained for silylated silica 1A. The resonance at -48.4 ppm is ascribable to silica atoms of the silicon nitride rotor.

are capable of forming crystallites. The low melting temperature of PDMS crystals in silica 2B suggests that the crystals were smaller than those in pure PDMS.

2. The Chemical Structure of Silylated Silicas Studied by Means of NMR Spectroscopy. The fraction of physically adsorbed PDMS chain units in the studied samples is small, as it will be shown in section 4.1.3. Since studied samples contain only a small fraction of residual silanol groups on the silica surface (see Table 1), this suggests that PDMS chains react with silanol groups at the silica surface. To determine the chemical structure of silylated silicas, ^{1}H and ^{29}Si NMR spectra were recorded. The ^{29}Si NMR spectrum obtained for silica 2A is shown as an example in Figure 2. The spectra obtained for the other samples were similar. The narrow resonance at -22.2 ppm and broad resonance at about -110 ppm are attributable to $-SiO(CH_3)_2-$ chain units and SiO_2, respectively. A broad shoulder at a lower field observed for the resonance at -22.2 ppm may be ascribable to the effect of the Si$-$O$-$Si bond angle or bond distance distribution of $-SiO(CH_3)_2-$ chain unit(s) adjacent to the silica surface. It is well-known that the ^{29}Si chemical shift is strongly affected by the geometry of the Si$-$O$-$Si bond.[22,23] The samples were found to contain only a small fraction of $-OSi(CH_3)_2-OH$ pendant groups, because no intensive ^{29}Si resonance corresponding to this group was observed at about -12 ppm.[24] *Thus, the grafted chains formed loops and/or interconnected neighboring silica particles, and the fraction of dangling chain ends is small.* This conclusion is supported by the ^{1}H NMR spectra obtained for the samples (Figure 3). The spectra reveal an intensive resonance for $-SiO(CH_3)_2-$ chain units at about 0 ppm and broad resonances at about 3 and 5$-$6 ppm, which are ascribable to residual silanol groups and adsorbed water molecules.[25] No signal was observed at 1.2 ppm corresponding to CH_3 hydrogen of $-OSi(CH_3)_2-OH$ pendant groups. Thus, the sample preparation causes depolymerization of the PDMS chain followed by its grafting to the silica surface. The mean length of the grafted chains, N_t, in the samples varies from four to eight Si$-$O bonds.

The fact that the $-SiO(CH_3)_2-$ chain units that were grafted to the silica surface and those in the middle portion of the chain show the same chemical shift in the ^{1}H and ^{29}Si spectra precluded the use of chemically selective NMR relaxation techniques for characterizing the PDMS$-$silica interfacial layer. We therefore performed nonselective low-resolution NMR relaxation experiments to characterize the structure of the PDMS grafted layer.

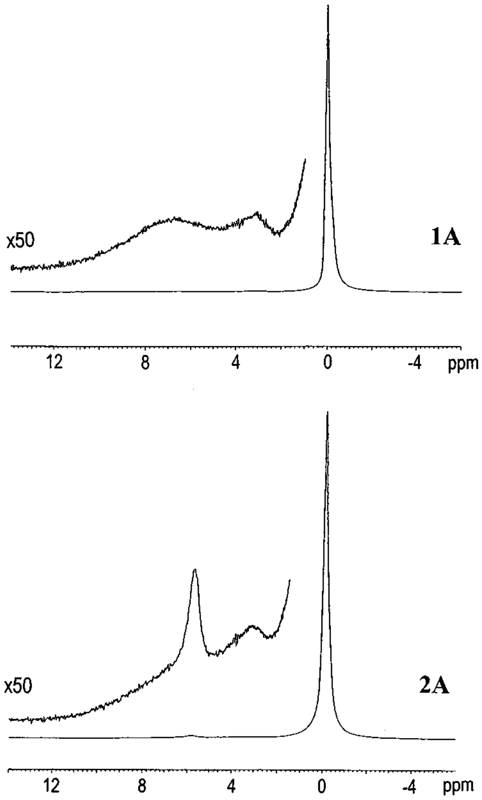


Figure 3. ^{1}H NMR MAS spectra obtained for the silylated silicas 1A and 2A.

3. The Structure of the Grafted Layer Studied in ^{1}H T_2 Relaxation Experiments. Proton NMR relaxation is caused mainly by dipole$-$dipole interactions between proton spins and by the averaging of these interactions due to molecular mobility. The T_2 relaxation is highly sensitive to chain dynamics involving large spatial-scale chain motion at temperatures above T_g. Since chain motion is closely coupled to the length of the grafted chains, grafting density and sterical constrains from surrounding chains, ^{1}H T_2 relaxation yields information on the structure of the grafted layer.

The decay of the transverse magnetization of two silica samples is shown in Figure 4. The T_2 decay for the samples as a whole consists of two distinct components with characteristic decay times, T_2, of 0.08 and 1$-$3 ms (Table 3). As mentioned above, the T_2 values are related to molecular mobility. The larger the amplitude and/or the frequency of chain motions, the longer the T_2 will be. The large difference in the decay time of these components suggests that these relaxation components are related to PDMS chain portions with significantly different local and large spatial scale chain mobility. The T_2 value of the component with the short decay time, $T_2^{\mathrm{in}} \approx 0.08$ ms, is in the range typical of polymers in the proximity of T_g. This component is ascribed to low-mobility chain portions adjacent to the silica surface—*the semirigid PDMS-silica* ***in****terface.*[18,19,26] Local chain mobility in the interface is strongly hindered due to chain anchoring to the silica surface and adsorption interactions of monomer units with the silica surface. It has previously been shown that T_2^{in} relaxation at the polymer$-$solid interface is not caused by the magnetic field gradients introduced by the filler particles.[18,21] This is also confirmed by the ^{1}H and ^{29}Si MAS spectra of the silica samples. If there were any magnetic field inhomogeneities at the silica surface, it

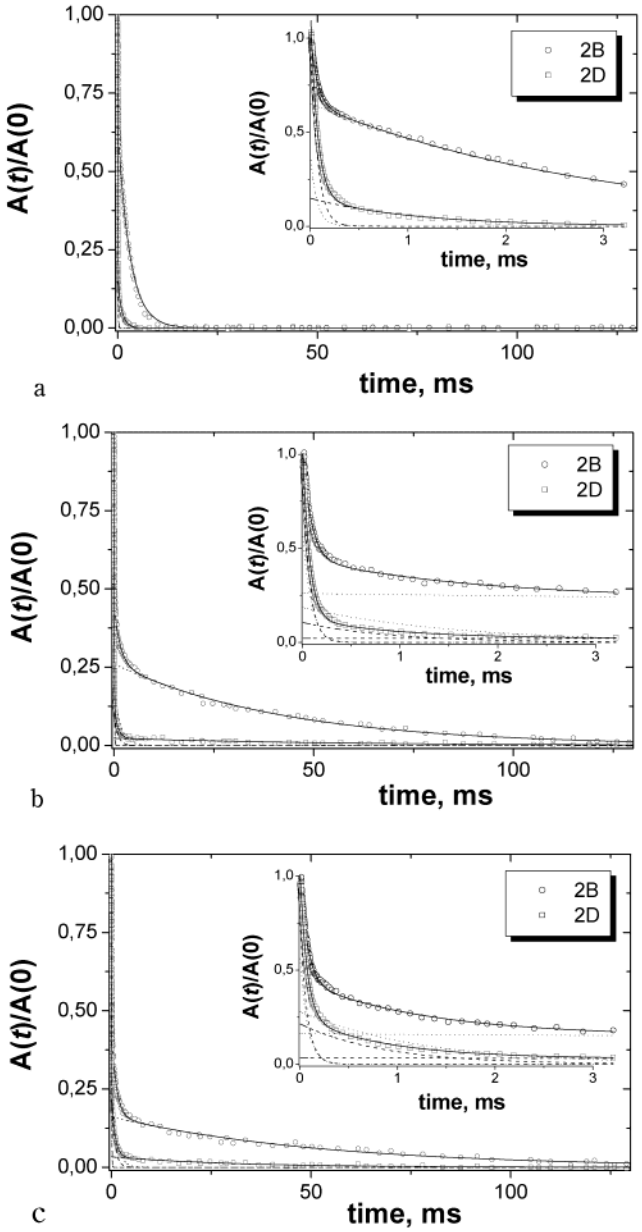


Figure 4. Decay of the transverse magnetization (points) at 40 °C measured for silicas 2B and 2D as a whole (a) and for the samples swollen in C_2Cl_4 (b) and those swollen in C_2Cl_4 in the presence of NH_3 (c). The decay was measured with the aid of the HEPS. The solid lines represent the result of a least-squares adjustment of the decay with a linear combination of two to three exponential functions. The dotted lines show the individual components. The initial part of the decay, measured with the aid of the SEPS, is shown in the insert on the right-hand side of the plots.

would be averaged out by the MAS frequency of 7.6 kHz. The fact that the spectra reveal significant line broadening suggests immobilization of grafted chains.

The component with the longer decay time, $T_2^{mo} = 1-3$ ms, presumably derives from *mobile chain portions outside the interface.* Since the statistical segment length of PDMS is about three $-SiO(CH_3)_2-$ units,[27] the rotational and translational chain mobility increases rapidly as the distance from the grafting site increases. This results in a sharp border between the interfacial and outer soft PDMS layer, as reflected by the distinct difference in T_2^{in} and T_2^{mo} relaxations. Long spatial scale chain mobility in the outer layer is to some extent hindered, as follows from the relatively small T_2^{mo} values that are comparable with those obtained for cross-linked elastomers of about 0.5−2 ms.[28] Constrained chain mobility outside the silica−PDMS interface is caused by anchoring of PDMS chains at both chain ends and probably by extension of the chain loops in the direction perpendicular to the silica surface reducing the number of possible chain conformations. A schematic representation of the grafted layer in relation to the relaxation parameters is shown in Figure 5.

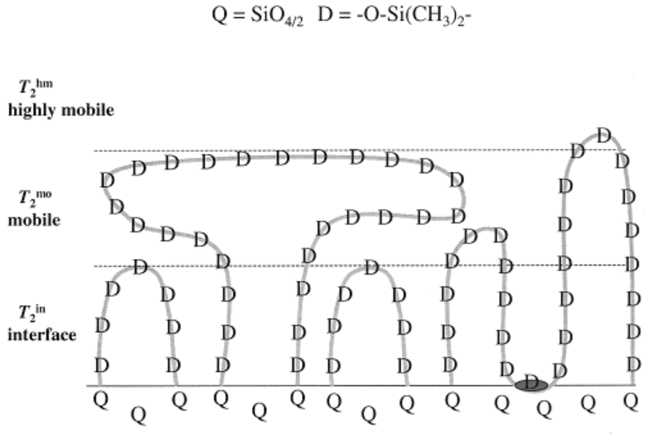
Table 3. T_2 Values, Expressed in μs, and the Relative Fraction of the Relaxation Components, Expressed in %, of the Samples as a Whole (*Bulk*), Samples Swollen in C_2Cl_4 (*sw*), and Samples Swollen in C_2Cl_4 in an Ammonia Atmosphere (*sw* + NH_3)

sample	T_2^{in}	T_2^{mo}	T_2^{hm}	$\%T_2^{in}$	$\%T_2^{mo}$	$\%T_2^{hm}$
			Silica 1A			
bulk	76	980		47	53	
sw	86	1030		53	47	
sw + NH_3	82	1300		50	50	
			Silica 2A			
bulk	81	1960		70	30	
sw	78	780	31 000	77	13	10
sw + NH_3	79	960	91 000	65	23	12
			Silica 2B			
bulk	75	3010	-	36	64	
sw	91	2570	96 000	54	19	27
sw + NH_3	78	1560	300 000	48	23	29
			Silica 2C			
bulk	84	2340		62	38	
sw	87	1000	43 000	72	12	16
sw + NH_3	87	1180	100 000	62	24	15
			Silica 2D			
bulk	75	1100		85	15	
sw	73	1300		87	13	
sw + NH_3	70	930	100 000	75	20	4

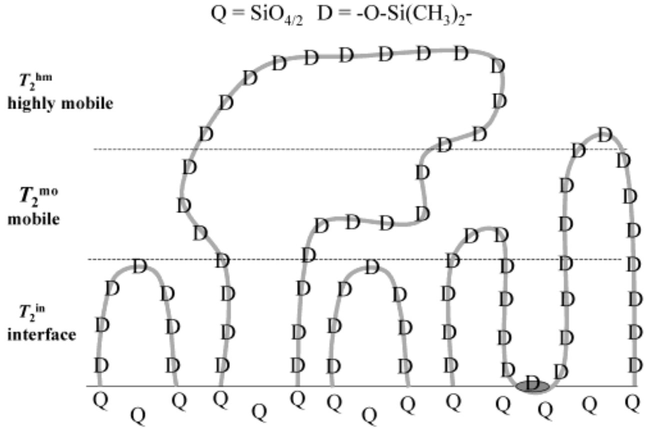
The third relaxation component with a characteristic time constant, T_2^{hm}, of 30−100 ms was detected in the swollen samples 2A−D. The T_2 values of this component are in the range typical of polymer solutions.[29] Since all the extractable PDMS had been removed in the exhaustive extraction of silylated silicas, this relaxation component can be ascribed to *highly mobile chain portions of long chain loops in the space above the densely grafted layer and/or in areas of low grafting density*. The relaxation parameters obtained for the samples swollen without and in the presence of ammonia (see Table 3) differ substantially. The fraction of highly mobile chain units and values of T_2^{hm} of ammonia-treated samples are larger compared to the original ones, corresponding to an increase in the mobility of grafted chains. Since ammonia is preferentially adsorbed on the silica surface,[18] its molecules cause desorption of physically adsorbed PDMS chains, resulting in the observed increase in chain mobility. Moreover, these changes suggest that areas with a relatively low grafting density which are available for physical adsorption of PDMS chains were present in silicas 2A−D.

The amounts of chain units at the PDMS−silica interface (1), in the densely grafted layer covering the interface (2), and in long chain portions in the space above the densely grafted layer (3) can be inferred from the values of $\%T_2^{in}$, $\%T_2^{mo}$, and $\%T_2^{hm}$, respectively (see Table 3).

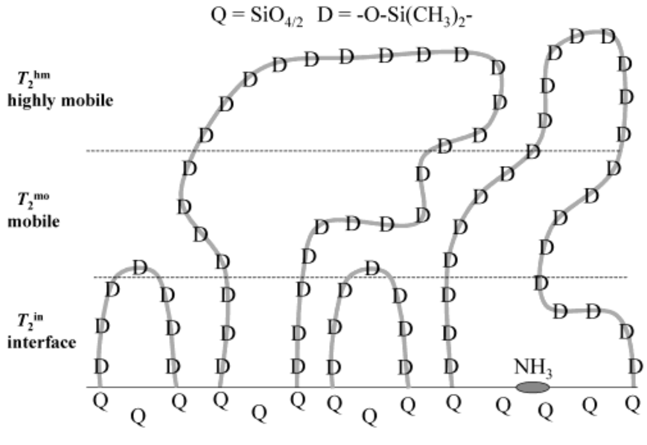
4. Molecular Structure of the Grafted Layer. The structure of the grafted PDMS layer can be generally characterized with the aid of the following parameters:



(1) Sample as a whole



(2) Sample swollen in C_2Cl_4



(3) Sample swollen in C_2Cl_4 in NH_3 atmosphere

Figure 5. Schematic representation of the structure of grafted PDMS layer at the surface of silicas 2A–D: (1) samples as a whole; (2) samples swollen in C_2Cl_4; (3) samples swollen in C_2Cl_4 in an ammonia atmosphere. A solid ellipse indicates adsorption bonds at the silica surface. Which chain portions are responsible for the T_2 relaxation components is indicated by dashed lines.

(1) molecular mobility (stiffness) in the interfacial layer; (2) the fraction of immobilized PDMS–silica interface and the interface thickness; (3) the fraction of immobilized interface deriving from *chain anchoring by means of chemical bonding of chain ends to the silica surface* and from *physical adsorption of PDMS at the silica surface* (the fraction of physically adsorbed chains is apparently related to the grafting density and its heterogeneity); (4) the number of monomer units along the chain in the interface which are immobilized due to chain anchoring to the silica surface and physical adsorption; (5) the chain length distribution of grafted chains; and (6) the fraction of long chain loops in the space above the densely grafted layer. The results of the NMR experiments in which these issues were studied are discussed below.

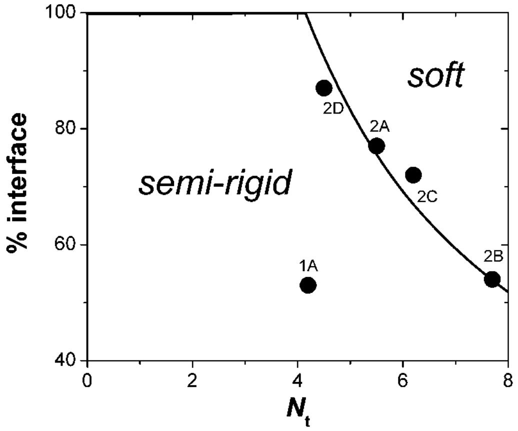


Figure 6. Fraction of PDMS–silica interface (%T_2^{in}) as a function of N_t determined for silica samples swollen in C_2Cl_4. The line represents the result of a linear regression analysis of the data obtained for samples 2A–D using eq 2. The correlation coefficient equals 0.90.

4.1. The PDMS/Silica Interface. 4.1.1. Molecular Mobility in the Interfacial Layer. It was found that chain mobility in the interfacial layer is not affected by the length of grafted chains and the presence of solvent, since the relaxation time measured for the PDMS/silica interface, T_2^{in}, was almost the same in all the samples (see Table 3). This suggests that the chain immobilization is caused by a loss of configurational entropy due to chain anchoring to the silica surface and by excluded volume effects from the silica surface and neighboring chains. It is known that grafted chains are the most elongated close to the surface when the surface area per polymer chain is much smaller than the characteristic size of an isolated chain,[30] which was the case in the studied samples. The small T_2^{in} value indicates that the chain units in the interfacial layer were substantially immobilized. The chain mobility at the interface is comparable with the mobility of pure PDMS at temperatures slightly above T_g.[18]

4.1.2. The Total Interface Fraction and Its Thickness. The fractions of the interfaces (%T_2^{in}) of the samples studied were found to differ substantially. The dependence of %T_2^{in} on the average length of PDMS chains is shown for samples swollen in C_2Cl_4 before and after ammonia treatment in Figures 6 and 7, respectively. In the case of the samples swollen in the presence of ammonia, %T_2^{in} was slightly smaller, suggesting chain desorption. Thus, chain immobilization at the silica surface is caused not only by chemical attachment of PDMS chains to the silica surface but also by physical adsorption. The results shown in Figures 6 and 7 clearly illustrate that the interfacial fractions of silicas 2A–D was strongly determined by the average length of the grafted chains and decreased with an increasing chain length. The slight increase in the interface content observed upon swelling (see Table 3) may have been caused by a reduction in the number of chain conformations in the interfacial layer due to some upward extension of chains from the silica surface in the swollen samples.

Table 4. Estimated Molecular Characteristics of the Grafted Layer[a]

molecular characteristics of silicas	1A	2A	2B	2C	2D
the average thickness of the grafted layer in the samples as a whole (r_g), nm	1.4	1.6	2.7	1.9	1.2
the interface fraction in the samples as a whole, $\%T_2^{in}$	47	70	36	62	85
the average thickness of the interface (r_{in}) in the sample as a whole, nm	~0.7	~1.1	~1.0	~1.1	~1.0
the interface fraction (in %) ascribable to[b]					
chemical grafting (f_{chem})	~94	~84	~89	~86	~86
physical adsorption (f_{ad})	~6	~16	~11	~14	~14
the fraction of highly mobile portions of chain loops and/or tails,[c] $\%T_2^{hm}$	~0	~12	~29	~15	~4

[a] The NMR data and structural characteristics of the samples presented in Tables 1 and 3 were used in estimating the molecular characteristics. To estimate the r_g and r_{in} values, complete coverage of the silica surface and a uniform thickness of the grafted layer and the PDMS−silica interface were assumed. [b] The estimated absolute error in a value of f_{ad} is about 2−3%. [c] Obtained for samples swollen in C_2Cl_4 in an ammonia atmosphere.

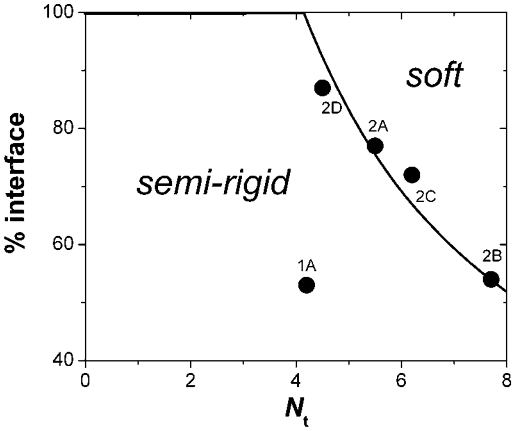


Figure 7. Fraction of PDMS−silica interface ($\%T_2^{in}$) as a function of N_t determined for silica samples swollen in C_2Cl_4 in the presence of NH_3. The line represents the result of a linear regression analysis of the data obtained for samples 2A−D using eq 2. The correlation coefficient equals 0.89.

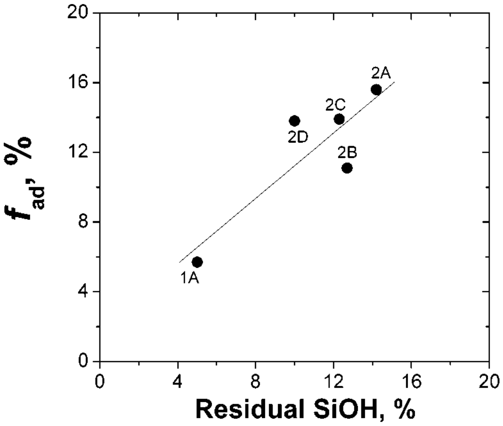


Figure 8. Fraction of the interface caused by physical adsorption (f_{ad}) as a function of the fraction of residual SiOH groups in silylated silicas. The line represents the result of a linear regression analysis of the data: intercept = 2 ± 4%; slope = 0.9 ± 0.3. The correlation coefficient and the standard deviation equal 0.87 and 2.2, respectively.

The thickness of the PDMS−silica interface was determined from the interface fraction and the specific surface of the hydrophilic silica, on the assumption of complete coverage of the silica surface and an interface with a uniform thickness. Taking into account the experimental error, the estimated average thickness of the interfaces of silicas 2A−D for all samples equals about 1 nm (see Table 4). The above results suggest a high degree of similarity in the structure of the interfaces in silicas 2A−D. If the grafting density was the only parameter determining the interfacial fraction, one would expect the largest interface fraction to be that of silica sample 1A, since this sample has the highest grafting density, as can be inferred from the number of residual SiOH groups at the silica surface (Table 1). However, the interface fraction of silica 1A is significantly lower than the fractions of silicas 2A, 2C, and 2D, as can be seen from Tables 3 and 4 and Figures 6 and 7. This suggests that the structures of the interfaces in silicas 2A−D differ substantially from the structure of that of silica 1A. This difference could be attributable to a difference in chain length distribution. Apparently, the molecular mobility of the short loops, which spread over the silica surface, is hindered to a greater extent than that of the long ones. The fact that the interfacial fraction in silicas 2A−D is significantly larger than the fraction in silica 1A could be due to a larger fraction of short chain loops in silicas 2A−D.

4.1.3. The Interfacial Fraction Caused by Physical Adsorption. The treatment of the swollen samples with ammonia resulted in a decrease in $\%T_2^{in}$. This decrease was of course caused by chain desorption due to preferential adsorption of ammonia at the silica surface.[18] The fraction of the interface resulting from physical adsorption (f_{ad}) was determined on the basis of the percentage of $\%T_2^{in}$ obtained for the swollen samples before $(\%T_2^{in})^b$ and after $(\%T_2^{in})^a$ ammonia treatment, suggesting that all the adsorption bonds were cleaved by ammonia:

$$f_{ad} = [(\%T_2^{in})^b - (\%T_2^{in})^a]/(\%T_2^{in})^b \qquad (1)$$

The density of physically adsorbed PDMS chain portions seems to be proportional to the number of residual silanol groups at the silica surface, as can be seen in Figure 8 and Tables 1 and 4.

4.1.4. Immobilization of Siloxane Chains Due to Chain Anchoring and Physical Adsorption. The number of immobilized $-SiO(CH_3)_2-$ chain units adjacent to the silica surface in silicas 2A−D was determined from the relationship between $\%T_2^{in}$ and the average number of Si−O bonds in grafted chains, N_t (see Figures 6 and 7). It can be easily shown that the fraction of immobilized chain units at the PDMS−silica interface, $\%T_2^{in}$, is related to the length of the grafted chains

$$\%T_2^{in} = 1 - (N_t - N_{ad})/N_t \qquad (2)$$

where N_{ad} is the number of immobilized $-SiO(CH_3)_2-$ chain units at the PDMS−silica interface and the N_t value corresponds to the total length of the chains grafted at one chain end, if present, and the half-length of chain loops and chains attached to neighboring silica particles. It is suggested that the length of the grafted chains does not affect N_{ad}. Extrapolation of this rela-

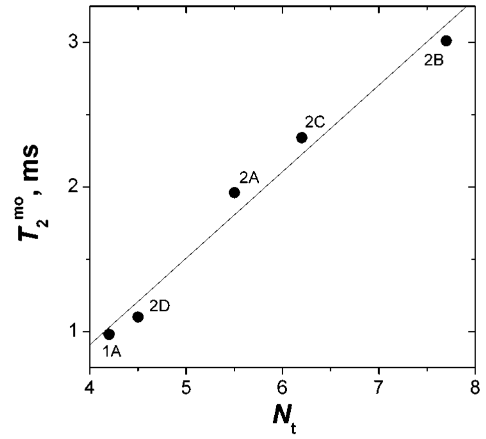


Figure 9. Dependence of T_2^{mo} on N_t determined for the samples as a whole. The line represents the result of a linear regression analysis of the data: intercept = −1.5 ± 0.3 ms; slope = 0.60 ± 0.5 ms. The correlation coefficient and the standard deviation equal 0.989 and 0.15, respectively.

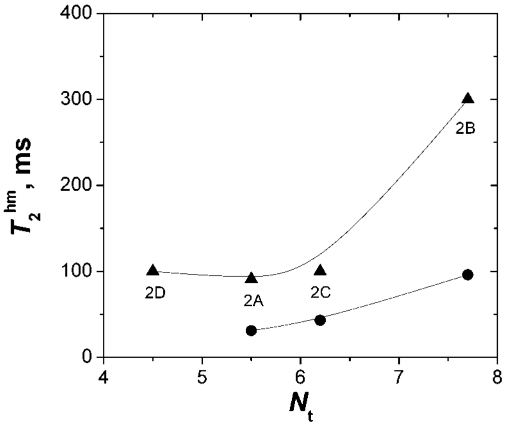


Figure 10. Dependence of T_2^{hm} on N_t determined for the swollen samples before (circles) and after (triangles) adsorption of ammonia. The solid lines have been included as guidelines.

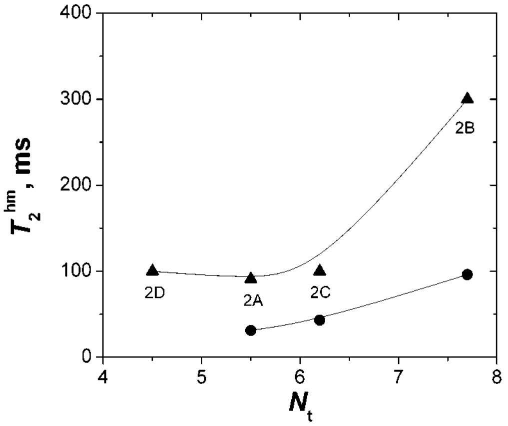


Figure 11. Dependence of $\%T_2^{hm}$ on N_t determined for samples swollen in the presence of ammonia. The line represents the result of a linear regression analysis of the data: intercept = −31 ± 4%; slope = 7.7 ± 0.6. The correlation coefficient and the standard deviation equal 0.994 and 1.4, respectively.

tionship to $\%T_2^{in}$ = 100% yielded the average number of immobilized chain units adjacent to the silica surface. The interface in the swollen samples 2A−D consisted of about 4.1 ± 0.2 $-SiO(CH_3)_2-$ chain units, whose mobility was hindered to a greater extent than that of the distant units. The number of low-mobility chain units decreased slightly to about 3.6 ± 0.2 upon ammonia adsorption. This was caused by desorption of chain portions from the silica surface and possibly by a decrease in chain−surface attractions.

The interface thickness of silica 1A was determined from the amount of interface and the average length of the grafted chains. The obtained value of about 2 $-SiO(CH_3)_2-$ chain units is smaller than the value obtained for silicas 2A−D. This agrees with the above suggestion of a smaller fraction of short chain loops in silica 1A than in the other samples.

4.2. Chain Length Distribution of Grafted Chains. The mobility of chain portions outside the interface increases with an increasing average chain length, as can be inferred from the dependence of T_2^{mo} on the chain length observed in the samples as a whole (see Figure 9). It is apparently caused by a decrease in chain elongation with an increasing distance from the surface.[30] With a decreasing chain length, T_2^{mo} would have reached the T_2^{in} value at about 3 $-SiO(CH_3)_2-$ bonds if a linear dependence of T_2^{mo} on the chain length is assumed. This value is in good agreement with the number of immobilized chain units in the interfacial layer estimated above (see Figures 6 and 7).

Due to the swelling, the T_2^{mo} relaxation component is split into two components, described by T_2^{mo} and T_2^{hm} values (see Table 3). The T_2^{mo} of the swollen samples is similar to that of the bulk samples. This component seems to originate from *the densely grafted layer outside the interface*. The chain mobility in this layer was hardly affected by the swelling, which can be explained as follows. In the samples as a whole, translational mobility of these chain portions was already hindered because they had extended upward from the silica surface and suffered steric hindrance from surrounding chains, which affected largely long-scale chain mobility. Swelling does evidently not lead to a significant increase in the number of possible chain conformations in the densely grafted layer. The T_2^{hm} relaxation component originates from *long chains outside the densely grafted layer and/or chains in areas of low grafting density*. The mobility and the relative fraction of highly mobile chain portions increased with an increasing average length of grafted chains in silicas 2A−D, as can be seen in Figures 10 and 11, respectively. The increase in mobility was apparently caused by a decrease in hindrance from anchoring sites with an increasing distance from the grafting site. The T_2^{hm} increased significantly upon adsorption of ammonia, whose molecules cleaved adsorption bonds between the silica surface and the PDMS chains.[18] The desorbed chain portions apparently suffered negligible steric hindrance from grafting sites and other segments in comparison with the short grafted chains.

The difference in the mobility of the long grafted chains in the samples as a whole and the swollen samples may have been caused by a change in the chain conformation upon swelling. The long grafted chains in the samples as a whole were flattened at the surface of the grafted layer due to van der Waals interactions with other PDMS chains. These chains probably take a so-called “pancake” configuration.[31] Swelling caused the long grafted chains to extend and to stick out of the densely grafted layer, resulting in increased chain mobility. These changes in polymer density profiles can be regarded as “pancake-to-brush” conformational transitions.[1,32]

4.3. The Structure of the Grafted Layer with Respect to Grafting Conditions. The structure of the grafted layer is largely determined by the employed grafting method, as can be inferred from Tables 1 and 4. It was found that a grafted layer in silica 1A has a dense structure, containing chains of a fairly uniform length in comparison with the other samples. Despite end-capping of the initial high-molecular-mass PDMS used in the sample preparation, the chains were broken into short fragments of about eight $-SiO(CH_3)_2-$ units. Apparently, silanol groups at the silica surface caused depolymerization of the PDMS chain. According to the N_t value of silica 1A, eight chain units correspond to thermodynamically the most stable length of chain loops. The silica samples prepared using method 2 showed a broad distribution of the length of grafted chains and a less uniform grafting density, suggesting incomplete chain depolymerization. The depolymerization was apparently favored by the long-term exposure of the silica−PDMS mixtures to a high temperature, as can be inferred from the structure of the grafted layer in silica 1A in comparison with that of samples 2A−D. It was rather surprising that silica 2D contained a large fraction of chemically attached PDMS chains despite the low temperature used during kneading (50 °C) and the large fraction of end-capped PDMS (86 wt %) used. Since a long kneading time was used during the preparation of this sample, this suggests that kneading causes significant mechanical breakdown of PDMS chains followed by the formation of chemical bonds between chain ends and silanol groups at the silica surface. Perhaps silanol groups at the silica surface facilitate PDMS depolymerization. Apparently, mechanical−chemical chain scission is determined by local shear forces during kneading,[33] the viscosity of the mixture, and the strength of silica−PDMS interactions, which are largely affected by temperature.[18]

Conclusions

Low-resolution ^{1}H NMR T_2 relaxation experiments provide valuable information on the structure of PDMS layers grafted onto silica surfaces. The method presents several advantages for the characterization of the structure of the grafted layer in materials of this type in relation to high-resolution NMR experiments because only a single resonance is observed for all chain units, which limits the execution of selective relaxation experiments. Our experiments showed that about four $-SiO(CH_3)_2-$ chain units adjacent to the grafting site form a semirigid PDMS−silica interface. When samples are swollen, NMR experiments can be used to determine the fraction of chain units within and outside the densely grafted layers, which is related to the chain length distribution of grafted chains. When swelling is performed in the presence of ammonia, such experiments can be used to determine the fraction of physically adsorbed chain units. Our experiments showed that the grafting conditions strongly affect the chain length distribution, the mean length of grafted chains and the fraction of residual silanol groups at the silica surface.

Acknowledgment. The authors are grateful to M. F. J. Pijpers for providing the results of the DSC experiments and greatly appreciate E. Currie's comments on the manuscript.

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(26) The contribution to this component from protons of residual silanol groups at the silica surface and from those of adsorbed water molecules is below a few percent, as follows from the ^{1}H NMR spectra shown in Figure 3, which is in agreement with the results of T_2 experiments using hydrophilic fumed silica. The amount of silica was taken to be equal to that in silylated silicas. The T_2 decay of the hydrophilic silica can be described by a single-exponential function with a characteristic decay time of 0.18 ms. The amplitude of the decay was a factor of 10 smaller than that of the silylated silicas despite the large fraction of surface silanol groups in hydrophilic silica that are sites for water adsorption.
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MA0119124