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Indication of Heterogeneity in Chain-Segment Order of a PDMS Layer Grafted onto a Silica Surface by ^{1}H Multiple-Quantum NMR

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ABSTRACT: The heterogeneity in segmental chain order of grafted polymers was investigated by ^{1}H multiple-quantum NMR. The measurements were performed on a series of samples of poly(dimethylsiloxane) (PDMS) layers chemically attached to the surface of hydrophilic silica. These grafted PDMS layers consist of partially immobilized chain segments at the PDMS−silica interface and mobile chain portions outside the interface which is supported by measurements of homonuclear double- and triple-quantum buildup curves. These curves reveal a bimodal distribution of the residual dipolar couplings along the PDMS chain. The segmental orientations detected in the interface and mobile regions are related to the average chain length and reflect the competing effects of the surface-induced orientation and chain conformations. The different behavior of the two chain fragments is evident from temperature-dependent measurements.

Introduction

The properties of polymers at interfaces are of growing technological importance due to extended use of surfaces modified by polymer films and polymer grafting and also due to the fundamental interest of surface effects on both polymer conformation and chain dynamics.[1,2] The preferred model polymer for such studies has been poly(dimethylsiloxane) (PDMS). The surface-induced orientational order of a monolayer thin film of this very flexible polymer, spin-coated on a polystyrene layer grafted on a silicon wafer[3] and deposited onto the walls of cylindrical pores,[4] was investigated by ^{2}H NMR spectroscopy. Recently, it was shown that the transverse ^{1}H relaxation is highly sensitive to the heterogeneous mobility of PDMS chains grafted onto a silica surface.[5] This NMR method allowed the distinction between a dense brushlike structure of the grafted layer containing chains of a fairly uniform length and a layer containing a significant fraction of long-chain loops outside the grafted layer. The mobility of the chain outside the interface was found to increase with increasing average length of the grafted chains.

One- and two-dimensional NMR spectroscopy has been used intensively in the past decade to measure homonuclear as well as heteronuclear residual dipolar couplings and corresponding dynamic order parameters in polymers and elastomers.[6,7] One of the model-free NMR methods applied to investigate the dependence of anisotropy of segmental motions on cross-link density, strain, and angular orientation is based on the multipolar spin states like double-quantum (DQ) coherences, triple-quantum (TQ) coherences, and dipolar encoded longitudinal magnetization (DELM).[8−10] In this paper, we investigate the distribution of the chain orientation of PDMS grafted onto hydrophilic silica by ^{1}H DQ and TQ coherences buildup curves. A bimodal distribution of the residual dipolar couplings is observed, and the effects of chain length and temperature are discussed.

Table 1. Structural Characteristics of Silylated Silicas[5]

sample	PDMS content, wt %[a]	av chain length, N_t	interface fraction, %[b]	mobile fraction, %[b]	T_g, K[c]
PDMS1	44.0	7.7	36	64	152
PDMS2	35.2	6.2	62	38	150
PDMS3	26.5	4.5	85	15	155

[a] Based on the carbon content. [b] Inferred from the relaxation components. [c] Temperature of the 50% increase in ΔC_p.

Experimental Section

Materials. A series of silylated silicas with different content of grafted PDMS and average chain length (N_t) were prepared at Wacker-Chemie GmbH (Burghausen, Germany). Details on the preparation can be found in ref 5. Surface modification was applied to hydrophilic fumed silica with a BET surface area of 300 m^2/g. The average number N_t of siloxane bonds per grafted site was derived from the PDMS content and the number of reacted SiOH groups. The N_t value 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 the investigated silylated silicas are presented in Table 1.[5]

NMR Measurements. The NMR experiments were performed at a ^{1}H frequency of 500.45 MHz on a Bruker DSX-500 spectrometer equipped with a temperature control unit using a 7 mm MAS probe head under static conditions. The ^{1}H DQ and TQ buildup curves were recorded with the pulse sequences presented in Figure 1. The 90° pulse length was 6.5 μs, and recycle delays of 1 s were used. The evolution time and the z filter delay were fixed to $t_1 = 2\ \mu$s and $\tau_f = 1$ ms, respectively.

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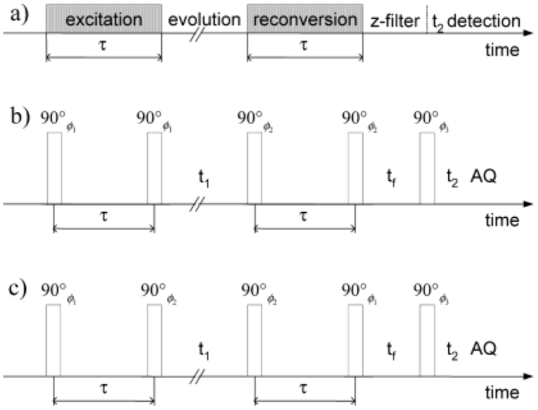

Figure 1. (a) General scheme for excitation of multiple-quantum coherences. (b) A five-pulse sequence for measuring double-quantum buildup curves. (c) A five-pulse sequence adapted for measuring triple-quantum buildup curves. The periods for excitation, evolution, reconversion, *z* filter, and detection are denoted by τ, t_1, τ, t_f, and t_2, respectively.

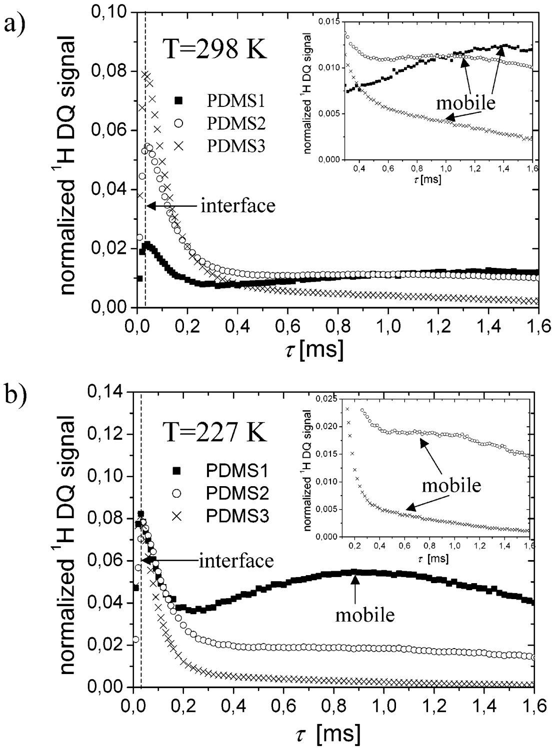

Figure 2. Proton DQ buildup curves of grafted PDMS samples recorded at $T = 298$ K (a) and $T = 227$ K (b). The region of the DQ buildup curves after the first maximum is enlarged in the insets.

A waiting time of 15 min assured temperature stabilization to ±0.1 °C and equilibration. The temperature calibration was done using the chemical shift difference of the two signals in methanol.[11]

Results and Discussion

The ^{1}H DQ and TQ buildup curves were measured at two temperatures, $T = 298$ K and $T = 227$ K, for the three grafted PDMS samples (see Table 1), and the results are shown in Figures 2 and 3. The data have been normalized to the integral intensity of the NMR signal after a 90° pulse. The buildup curves display two maxima. The first maximum shows a relatively sharply defined value of the excitation and reconversion time τ. The second maximum at longer τ values is more difficult to identify in sample PDMS3 and less pronounced in sample PDMS2 due to the small amount of the mobile fraction and the broadness of the signal. Nevertheless, the second maximum is enhanced at lower temperature due to reduced mobility and therefore increasing residual dipolar coupling. The maximum at short τ values is due to the segments at the interface, and those present at longer τ correspond to the mobile fractions of the grafted PDMS chains. The first maximum occurs at the same τ value for the three samples, indicating the same chain immobilization in the interface of all three samples. The immobilization is caused by a loss of conformation entropy due to chain anchoring to the silica surface and by excluded-volume effects from the silica surface and neighboring chains. Thus, the averaged residual dipolar couplings of the interface have the same values independent of N_t. These results are both reflected in the ^{1}H DQ as well as in the ^{1}H TQ buildup curves.

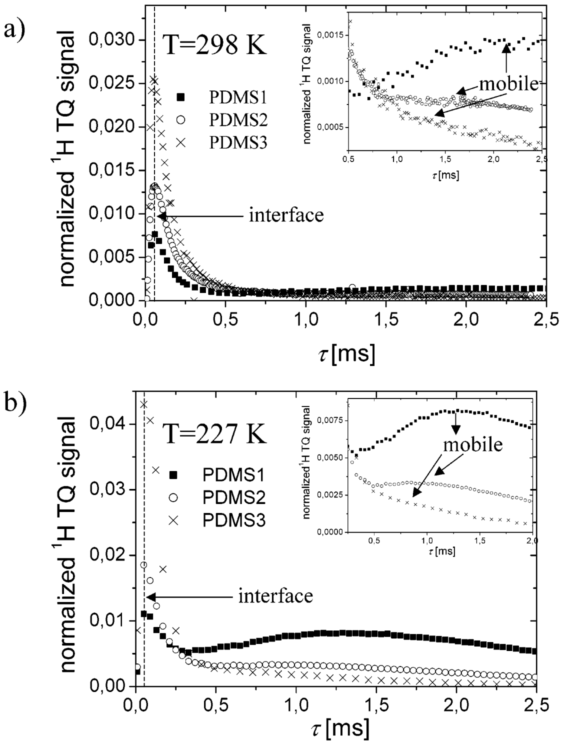

Figure 3. Proton TQ buildup curves of grafted PDMS samples recorded at $T = 298$ K (a) and $T = 227$ K (b). The region of the TQ buildup curves after the first maximum are enlarged in the insets.

The positions of the second maximum of the three samples are also indicative of the anisotropy of chain motions outside the interface. Assuming the same thickness of the interface in all three samples, we deduce that the fraction of the mobile chain fragments decreases from sample PDMS1 to PDMS3. This results in a shorter τ value for the position of the second maximum for sample PDMS3 vs samples PDMS2 and PDMS1, which can be seen in the DQ as well as the TQ buildup curves. For sample PDMS3, this leads to the observation that the second maximum can be discriminated from the first as a soft shoulder only.

Temperature-dependent measurements of the DQ buildup curve of sample PDMS1 show some interesting features, as can be seen in Figure 4a for the maximum of the rigid component and Figure 4b for the maximum of the mobile component. For the mobile component

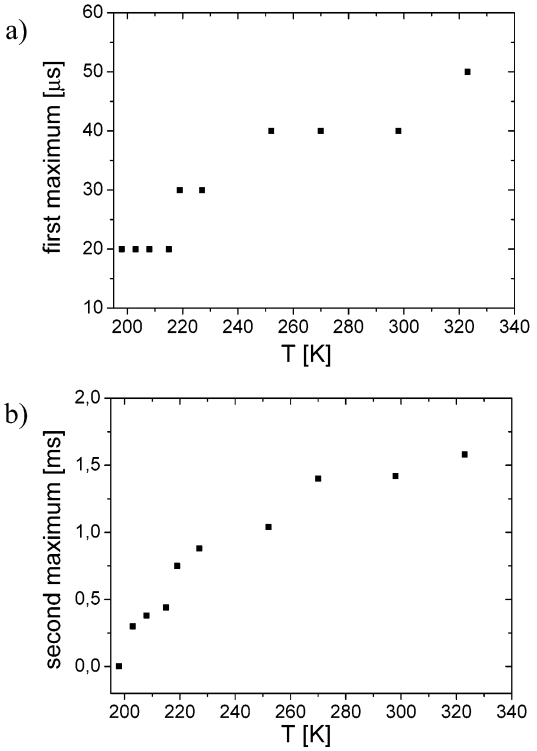

Figure 4. Excitation/reconversion time τ for first (a) and second (b) maximum of the DQ buildup curves (cf. Figure 2) as a function of the temperature.

there is a continuous decrease of the corresponding excitation time due to the reduced mobility with decreasing temperature. Finally, at temperatures below 198 K only one maximum can be seen. For the maximum of the rigid part, there is a rather constant position of the maximum down to about 240 K. A fast decrease in the position of the first maximum is observed around 220 K which is due to the crystallization of the PDMS chains of this sample.[5] A further decrease of the excitation-time maximum takes place below $T = 203$ K. At these temperatures the mobility of the chains is reduced in such a way that the DQ buildup curve coalesces into one maximum. In this case, the whole chain appears to be immobile at the time scale of the NMR experiment of about 10^{-5} s. In general, residual dipolar couplings are affected by fast local motions as well as slow chain motions with correlations times smaller than the time scale of the NMR experiment.

Conclusions

A bimodal distribution of the segmental-chain orientation corresponding to the interface and the mobile regions of PDMS chains grafted onto silica was detected by ^{1}H multiple-quantum NMR spectroscopy. The size of the interface is found to be independent of the total length of the PDMS chains. A broad distribution of segmental orientation prevails in the mobile region, and the segmental mobility is proportional to its fraction and therefore to the chain length. At lower temperatures the mobility decreases until at $T = 198$ K the whole chain appears to be immobile. The orientation distribution function of the segments can be determined for the grafted chains of PDMS on the basis of the experiments described above. Work along this line is in progress in our laboratory.

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