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Phase Behaviour of Poly(di-*n*-decylsilane)

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Summary. The phase behaviour of poly(di-*n*-decylsilane) (*PD10S*) was investigated by DSC and ^{29}Si as well as ^{2}H solid state NMR spectroscopy. For ^{2}H NMR experiments, the polymer was deuterated in the α-position of the side chains. Depending on the thermal history of the sample, DSC shows two transitions at 303 and 320 K with varying intensity ratio. Above 320 K, only the conformationally disordered mesophase exists. NMR spectra prove the existence of two crystalline states **I** and **II**. State **I** is either a pure phase with a complex backbone structure or a superposition of several crystalline modifications, whereas state **II** probably corresponds to a single phase with transoid backbone conformation. Either state can be obtained separately.

Keywords. Polysilanes; Poly(di-*n*-decylsilane); Phase behaviour; Mesophase; ^{29}Si solid state NMR; ^{2}H solid state NMR.

Phasenverhalten von Poly(di-*n*-decylsilan)

Zusammenfassung. Das Phasenverhalten von Poly(di-*n*-decylsilan) (*PD10S*) wurde mittels DSC und ^{29}Si- sowie ^{2}H-Festkörper-NMR-Spektroskopie untersucht. Für die ^{2}H-NMR-Experimente wurde das Polymer in der α-Position der Seitenketten deuteriert. Abhängig von der thermischen Vorgeschichte der Probe zeigt die DSC zwei Übergänge (bei 303 und 320 K) mit variablem Intensitätsverhältnis. Oberhalb von 320 K existiert nur die konformativ ungeordnete Mesophase. NMR-Spektren beweisen die Existenz von zwei kristallinen Zuständen **I** und **II**. Zustand **I** ist entweder eine reine Phase mit komplexer Struktur des Rückgrats oder eine Überlagerung mehrerer kristalliner Modifikationen, während Zustand **II** wahrscheinlich einer reinen Phase mit transoider Rückgratkonformation entspricht. Jeder Zustand kann separat erhalten werden.

Introduction

Polysilanes (polysilylenes) with organic side chains, (-SiR_2-)$_n$, are linear inorganic-organic hybrid polymers with unusual properties due to their one-dimensional Si chains. They exhibit, for instance, strong UV absorptions and photoconductivity [1, 2]. Furthermore, poly(di-*n*-alkylsilanes) with side chains in the range of 4 to 14 methylene units exhibit an order-disorder transition from the crystalline phase to a hexagonal, columnar mesophase (μ) with conformational disorder, resulting in peculiar changes in their electro-optical properties [1]. Whereas the lower

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homologues, poly(di-*n*-propylsilane) (*PD3S*) to poly(di-*n*-hexylsilane) (*PD6S*), show only one crystalline modification at atmospheric pressure and therefore only one phase transition from crystalline to mesophase [2], polysilanes with longer alkyl side chains (from 8 to 10 methylene units) show two phase transitions with an intermediate phase below the mesophase [1, 3]. In poly(di-*n*-decylsilane) (*PD10S*) the two phase transitions occur at approximately 308 K and 328 K [1, 4]. At least two different crystalline phases with λ_{max} of 350 and 378 nm have been observed for *PD10S* [1]; the solid state composition was reported to vary with molecular weight and thermal history. Further heating into the mesophase leads to a UV absorption with λ_{max} of 318 nm.

Some disagreement still exists in the literature regarding the structure of the low temperature (**I**) and the intermediate phase (**II**) of *PD10S*. Based on the UV absorption maxima, *van der Laan et al.* [4] assume an all trans (TT) backbone structure and a TGTG′ structure for the low-temperature and the intermediate crystalline phase, respectively. *KariKari et al.* [5], however, report only on one phase, probably the low-temperature phase, for which they find X-ray patterns indicative of a TGTG′ or possibly a T_3GT_3G' conformation. Solid state NMR studies, which can contribute to the elucidation of the crystal structure, have, to our knowledge, not been reported.

We selected *PD10S* (besides other poly(di-n-alkylsilanes)) for an ongoing systematic study of the molecular dynamics of polysilanes by solid state NMR and of their polymorphism at elevated pressure for several reasons. First of all, *PD10S* exists in different crystalline phases at atmospheric pressure. Furthermore, of the known alkyl substituted polysilanes it exhibits the highest value of λ_{max}, and its charge carrier mobility is extraordinarily high [4]. For our deuteron experiments, a sample of *PD10S* deuterated in the α-position of the side chains was synthesized. First ^{2}H and ^{29}Si solid state NMR results on the phase behaviour of *PD10S* are presented in the following.

Results and Discussion

Figure 1 shows differential scanning calorimetry (DSC) traces of *PD10S* samples with different thermal and crystallization histories. After conventional precipitation and fractionation, *PD10S* shows a DSC trace (2nd heating run) as represented by curve *a* of Fig. 1 with a dominating first phase transition at 304.1 K ($\Delta H = 11$ kJ/mol) followed by a minor transition at 321.7 K with a much smaller transition enthalpy of $\Delta H = 2$ kJ/mol. When a sample is annealed at 313 K between the two transitions and slowly cooled to 243 K, the subsequent heating runs show that the low temperature transition vanishes. After annealing for 17 h, both transitions are still observable, but after annealing for 24 h only the transition at higher temperature remains ($T = 322.9$ K, $\Delta H = 10.6$ kJ/mol) as shown in curve *b*. A similar DSC trace with only the high temperature transition at $T = 323.9$ K ($\Delta H = 11.7$ kJ/mol) is observed for the first heating run when the sample is not precipitated but slowly crystallized from solution at elevated temperature (curve *c*). When either type of sample with only one transition, precipitated and annealed or slowly crystallized, is cooled rapidly (at 2 K/min) from the mesophase, the subsequent heating run shows two transitions of similar magnitude.

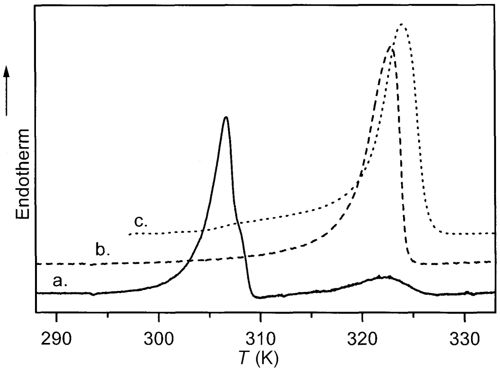

Fig. 1. DSC traces of *PD10S*; *a*: fractionated polymer sample, 2nd heating run; *b*: fractionated sample after annealing for approximately 24 hours; *c*: slowly crystallized sample as received (1st heating run)

Figure 2 depicts ^{29}Si CP-MAS solid state NMR spectra. The spectra *a–d* were obtained for a fractionated sample upon heating. The first spectrum at 260 K (Fig. 2a) corresponds to the low temperature crystalline state which is referred to as state **I** in the following. It shows three resonance lines at −19.7, −22.5, and −30.8 ppm which are unusually narrow as compared to the spectra of other polysilanes. The spectrum at 303 K (Fig. 2b) is a superposition of the three-line spectrum of state **I**, a broad resonance line at −20.7 ppm attributed to a second crystalline state (**II**), and the sharp resonance line of the mesophase at −24.6 ppm. It is commonly observed for polysilanes and other polymers with similar mesophases that the phase transitions are broad and that the resonances of the higher-temperature phases are observed well below the temperatures of the DSC peaks. Therefore, it is not surprising to find the mesophase peak already at 290 K upon heating (spectrum not shown). At 305 K (Fig. 2c), the low-temperature state **I** has disappeared, and only the peaks of the mesophase and of state **II** remain. A spectrum of the pure mesophase at 322 K is shown in Fig. 2d. Very slow crystallization from the mesophase during cooling at a rate of 0.5 K/h down to 260 K yields a crystalline *PD10S* consisting only of state **II** as can seen from Fig. 2e. In a series of fast crystallization experiments (not shown), spectra analogous to Fig. 2a were obtained. This shows, in agreement with the DSC results, that the low-temperature state can be recovered.

^{2}H NMR spectra of fractionated α-deuterated *PD10S* are shown in Fig. 3. The spectrum at a temperature of 255 K, well below the first phase transition, is a typical powder spectrum with a quadrupole splitting ($\Delta\nu$) of about 121 kHz, evidencing that the polymer sample is immobile except for small amplitude motions of the side chains. Above the transition to the mesophase at 322 K, motionally narrowed powder spectra are obtained with splittings of about 23 kHz. A splitting of this size is characteristic of the mesophase of polysilanes [6, 7]. The spectral shape reflects the axial symmetry of the molecular motions, and the narrow width proves the highly dynamic nature of both side and main chains. The spectrum recorded at 304 K, near the transition to the intermediate state, is a superposition of several fractions: the almost rigid one with a splitting of 119 kHz

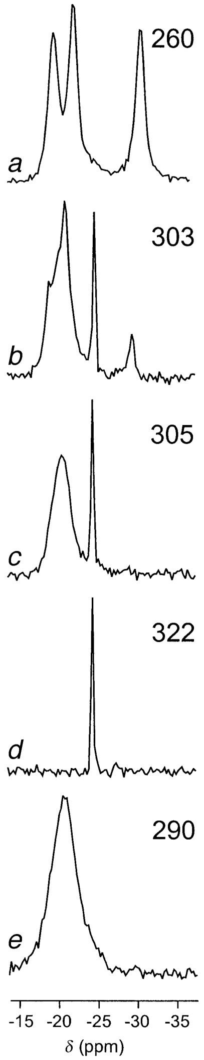

Fig. 2. ^{29}Si CP/MAS NMR spectra; *a–d*: variable temperature series of fractionated *PD10S* upon heating; *e*: after slow cooling from the mesophase (temperatures in K)

at this temperature (probably state **I**), a more mobile fraction with a reduced quadrupolar splitting of about 85 kHz (probably state **II**), the beginning mesophase ($\Delta\nu$ of 23 kHz) , and finally a small amount of an amorphous fraction giving rise to the narrow isotropic peak in the center. The spectra in the mesophase are similar for all polysilanes studied so far [6, 7], indicating that the dynamic processes are the same in all compounds. These spectra are motionally narrowed by a factor of about 1/5, making evident that the Si chain is also involved in the motions. If the polymer backbone were rigid and free rotation of the side chains were the only motion, the spectrum would be narrowed by a factor of only about 1/3 compared to the rigid powder pattern. Both side chains and main chain are conformationally disordered and mobile in the mesophase.

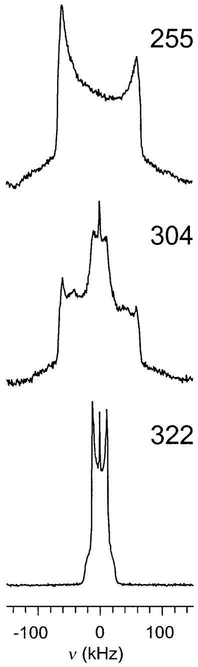

Fig. 3. ^{2}H NMR spectra of α-deuterated *PD10S* (temperatures are given in K)

DSC and NMR data together clearly show the existence of two different crystalline states below the mesophase. Either one can be obtained separately: the low-temperature state (**I**) by rapid cooling from the mesophase, and the intermediate-temperature state (**II**) by slow crystallization from the mesophase or by annealing at temperatures where the intermediate state and the mesophase coexist. Obviously, the formation of state **I** is favoured kinetically, whereas state **II** is the thermodynamically more stable form, at least at intermediate temperatures.

Regarding the structure of the two distinct states, ^{29}Si NMR spectroscopy provides important information. The three resonances of state **I** rule out a single phase with a TT backbone conformation. The spread in the chemical shifts of the three peaks is too large to be accounted for by mere intermolecular packing effects. The present data, however, do not allow to decide whether or not state **I** corresponds to a single phase. Assuming a single phase, at least three non-equivalent Si sites must exist in the elementary cell. A simple sequence such as TGTG′ or T_3GT_3G' can probably be ruled out because it does not account for the observed number of peaks with different chemical shifts. Alternatively, the three NMR peaks may arise from two or even three coexisting crystalline modifications. The spectra of state **II** are very similar to those of *PD6S* with respect to peak position and width. For this compound, only one modification with a TT backbone conformation is known [8–10]; therefore, we assign a single phase with transoid structure to state **II**. X-ray experiments, which are expected to allow a more precise determination of the phase behaviour, are presently underway.

Experimental

Dichlorodidecylsilane was polymerized using the well-known *Wurtz*-type coupling reaction with Na [1]. For the polymer with α-deuterated side chains, a deuterated monomer was prepared in a four-step synthesis, starting from decanoic acid anhydride which was reduced with $LiAlD_4$. The resulting α-deuterated decanol was converted to the corresponding *n*-decyl bromide using aqueous HBr; from this, the respective *Grignard* derivative was prepared. A *THF* solution of the *Grignard* compound was added to a solution of $SiCl_4$ in pentane to yield the α-deuterated dichlorodidecylsilane monomer. The crude polymers were precipitated twice from methanol/*THF* and fractionated with methanol from toluene solution to obtain polymers with a monomodal mass distribution. Alternatively, slowly crystallized samples of *PD10S* were prepared by dissolving 0.01–0.02 weight% polymer in cyclohexanol at 433 K. After cooling slowly within several hours, the turbid solution was filtered through 0.45 μm PTFE filters, and the precipitate was dried *in vacuo*. The poly(di-*n*-decylsilanes) were characterized by ^1H, ^{13}C, and ^{29}Si as well as two-dimensional ^1H–^{13}C COSY NMR spectroscopy in toluene-d_6 solution on a Bruker ARX 300 MHz spectrometer. Gel permeation chromatography (GPC), calibrated to polystyrene standards, yields a molecular weight M_w (weight average) of about 200000 g/mol with $M_w/M_n = 1.6$ for the fractionated non-deuterated sample.

Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC 7 at scan rates of 1 K/min. All samples were subjected to a first heating and cooling cycle before data acquisition unless indicated otherwise. Variable temperature ^2H and magic angle spinning (MAS) ^{29}Si solid state NMR measurements were carried out on a Bruker MSL 300 MHz spectrometer at resonance frequencies of 46.073 MHz and 59.625 MHz for ^2H and ^{29}Si, respectively. Deuteron spectra were obtained with a quadrupole echo pulse sequence with 90° pulses of 3.9 µs and a recycle delay of 3 s. 1024 scans were averaged. ^{29}Si MAS spectra were measured using the cross-polarization (CP) technique. A double-bearing MAS probe at spinning rates of about 2.5 to 3 kHz was used. The 90° pulse length was set to 4.5 µs with a CP contact time of 3 ms and a recycle delay of 4 s. 512 spectra were accumulated. ^{29}Si chemical shifts (referenced to *TMS*) were calibrated with Q_8M_8 (Bruker).

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