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Solid-State NMR Studies on the Molecular Structure and Dynamics of Poly(diethylsiloxane) Polymorphs†

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ABSTRACT: Molecular structure and segmental motion of different crystalline modifications of high molecular weight poly(diethylsiloxane) have been investigated by variable-temperature MAS ^{13}C and ^{29}Si NMR experiments. The observations were discussed in correlation to thermodynamic data. Cooperative changes of the motional state of the molecular backbone and the side chains are observed at the solid transitions detected by differential scanning calorimetry (DSC) experiments. Structural differences of the α- and β-polymorph are indicated. Annealing experiments allow determination of the β-modification as the equilibrium modification. The stepwise loss of long-range order at the onset of different motional processes, which results in the formation of a "liquid crystal" type phase of these highly flexible long chain molecules, is discussed with respect to the amphiphilic constitution of poly(diethylsiloxane) having an inorganic backbone substituted by organic side groups.

Introduction

In a recent review we discussed experimental data and general characteristics of the mesomorphic phases (i.e., neither fully ordered like a rigid crystal nor without long-range correlation in the molecular packing like an amorphous melt or glass) of highly flexible chain molecules.[1] Because of the lack of a rigid, nonspheric mesogenic subunit in the molecular structure and the fact that the molecules are typically packed in a hexagonal cylinder lattice, we distinguished those mesophases as a matter of principle from liquid crystals. Featuring the most important aspect of the partially disordered structure we described them according to B. Wunderlich as conformationally disordered crystals, i.e., Condis crystals.[2]

Solid-state NMR experiments showed the dynamic nature of the disordering. It has been possible to monitor the type and the changes of segmental motions within the mesomorphic phase and at the corresponding phase transitions for typical examples, i.e., poly(*trans*-1,4-butadiene),[3,4] cycloalkanes,[5–7] and *n*-alkanes.[8,9] The results may be summarized by describing those mesophases as a state where the molecules are arranged in regularly packed virtual cylinders, in which, however, they can move surprisingly unrestricted. Fast liquidlike conformational interconversion processes of carbon–carbon single bonds and, in addition, translational diffusion are characteristic. This reptational motion of chain molecules through the lamellae can explain the formation of extended chain crystals.[10,11]

In addition to the compounds mentioned above, which consist of linear nonpolar molecules, there is a second class of highly flexible molecules for which mesomorphic or even liquid crystalline behavior has been reported. These are various polyphosphazenes,[12–14] poly(di-*n*-alkylsilanes),[15,16] poly(diethylsiloxane),[17–27] and poly(dipropylsiloxane).[28,29]

Table I
Glass Transition, Melting, and Solid–Solid Transition Temperatures of Inorganic–Organic Hybrid Polymers

	transition temp, K			
polymer	T_g	T_d	T_m	ref
poly(di-*n*-hexylsilane)		315	>453	15, 16
poly(diethylsiloxane)	134	206/280 214/290	319	22
poly(dipropylsiloxane)	164	218/333	479	17, 24
poly[bis(trifluoroethoxy)-phosphazene]	207	363	515	13
poly[bis(*p*-chlorophenoxy)-phosphazene]	273	442	629	12

It is common to these compounds that they consist of an inorganic backbone that is symmetrically substituted by organic side chains. In general, the rotational barriers for bonds of second- and third-row elements are low. Thus in most cases, the molecular backbone and often also the side chains of polyphosphazenes, polysiloxanes, and polysilanes are highly flexible. This flexible character is demonstrated by the very low glass transition temperatures listed in Table I, together with the solid–solid transitions reported in the literature.

In the present paper we compare data from variable-temperature NMR and differential scanning calorimetry experiments in order to get a detailed picture of the conformations, conformational changes, and variations of the motional state of PDES at the different transitions.

Experimental Section

Polymerization. Hexaethylcyclotrisiloxane was obtained from Petrarch Chem. The monomer was used as supplied. The PDES sample was prepared by ring-opening polymerization of hexaethylcyclotrisiloxane in the presence of KOH as initiator.[30] High molecular weight fractions were seperated from oligomers by repeated precipitation in methanol.

For gel permeation chromatography, styragel columns with a length of 30 cm and a diameter of 7.7 mm were used. The particle size was 10 μm; the pore size was 10^6, 10^5, 10^4, and 10^3 Å. The temperature was 300 K and toluene was used as solvent. GPC

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† Dedicated to Prof. Dr. P. Rempp at the occasion of his 60th birthday.

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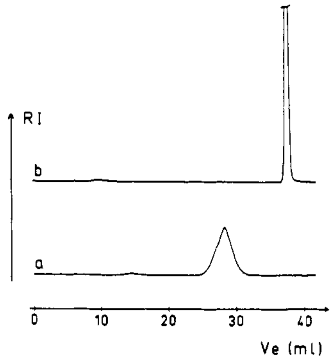


Figure 1. GPC trace of poly(diethylsiloxane) after purification from low molecular weight fractions (a) in comparison to the GPC trace of hexaethylcyclotrisiloxane (b), recorded at room temperature in toluene.

traces of the polymer and the hexaethylcyclotrisiloxane are presented in Figure 1 to demonstrate the absence of low molecular weight cyclic siloxanes in the polymer used for the DSC and NMR investigations. The eluation volumes correspond to an apparent molecular weights o M_w = 81 000 and M_n = 50 000 according to the calibration by standard polystyrenes.

The actual number-average molecular weight was M_n = 93 000, as obtained from osmotic pressures by means of a Hewlett-packard 502 high-speed membrane osmometer at 300 K in THF.

The pure β-polymorph was prepared by several cooling and heating cycles between 265 and 278 K, where the cooling rate was 1 K/min. The sample with the highest fraction of the α-modification was prepared by quenching the sample from the mesophase with a liquid butane/propane mixture, cooled with liquid nitrogen.

Calorimetry. For DSC measurements, a Perkin-Elmer DSC 7 was used. The instrument was calibrated with high-purity samples of indium, gallium, and cyclohexane. The transition temperatures were recorded with a heating rate of 10 K/min. Typically the sample weight was chosen between 0.5 and 1 mg. Temperature accuracy was better then ±1 K. Within these limits, corrections for heating rates were neglegible due to the small samples. Transition temperatures are given as recorded. The transition enthalpies determined by numerical integration of the transition peaks showed variations of less then 5%. The transition entropies were calculated by assuming equilibrium, i.e., $T_{tr}\Delta S_{tr} = \Delta H_{tr}$.

NMR. High-resolution solid-state ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker CXP 300 spectrometer at 75.47 and 59.63 MHz, respectively. A Bruker double-bearing MAS probe that was modified for variable-temperature experiments was used. Silicone nitride ceramic cylinders were used as rotors. Thus, quenching could be done within the MAS rotor. Line narrowing was achieved by high-power decoupling and magic angle sample spinning. Spinning rates were set to 2200–3000 Hz. Two different pulse sequences were used to generate the spectra. The usual spin–lock cross-polarization sequence[31] was applied for the spectra in the low- and the high-temperature phase; the 90° pulse (3.0 μg for ^{13}C and 3.9 μs for ^{29}Si) was followed by a mixing time of 1–4 ms and an acquisition time of 30–150 ms. The spectra of the mesophase and of the melt were obtained without cross polarization, a simple 90° pulse in combination with high-power proton decoupling was applied. Delay times between 10 to 600 s were chosen to be at least five times as long as T_1 to ensure complete relaxation between each pulse experiment.

For the assignment of the ^{13}C signals to methylene or methyl groups, the standard cross-polarization pulse sequence was employed with a delay time of 100 μs between the mixing and the acquisition period. Thus, the methylene resonance was suppressed nearly totally.[32]

For T_1 measurements (in the μ-phase and the melt), the inversion recovery pulse sequence[33] was applied and the delay time between the 180° and 90° pulse was varied systematically.

Deconvolution of the signals was carried out on a DEC Microvax GPX2, by fitting pure Lorentzians.

The ^{13}C chemical shifts were determined by comparison with the methylene signal of crystalline (orthorhombic) linear poly(ethylene) which was set to 32.81 ppm relative to TMS[34] and considered to be temperature independent. The ^{29}Si chemical shifts were determined by comparison to the spectrometer frequency referring to TMS at room temperature. Temperatures were measured by means of a thermocouple adjacent to the rotor. They were less accurate (±3 K) then the DSC temperatures.

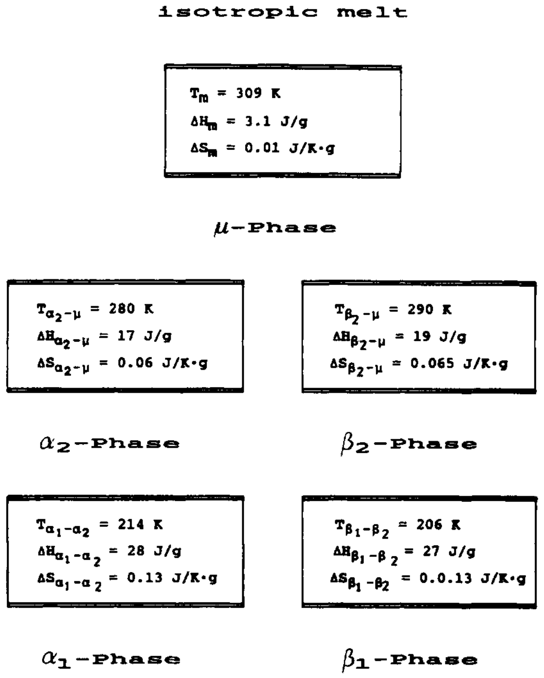


Figure 2. Polymorphism and melting of poly(diethylsiloxane).

Calorimetry

The thermal behavior of PDES is schematically summarized in Figure 2. The transition temperatures and heats of transition were obtained by DSC on heating the samples. The agreement to the data given by Papkov and Tsvankin[23,24] is good. High molecular weight poly(diethylsiloxane) (PDES) exists in two crystalline polymorphs, α and β. Each of them undergoes a disordering transition from α_1 to α_2 and from β_1 to β_2, respectively. Both polymorphs show an additional transition below the melting point, to a phase μ, which is also referred to as the α_m-phase.[23,24] The μ-phase is reported to be the same irrespective of whether it was reached upon heating the α- or the β-modification or on cooling from the melt.[23,24,26] The α_2–μ transition occurs at 280 K, the β_2–μ transition at 290 K. The μ-phase has a distinguished mesomorphic character. The material is birefringent and thus anisotropic. As it can be sheared like a viscous liquid, it has been described as liquid crystalline or as viscous crystalline.[18-22] The occurrence of this mesophase depends strongly on molecular weight. Its formation has not been observed for low molecular weight PDES samples.[25]

The DSC traces in Figure 3 demonstrate variations in the melting behavior, which result from different thermal histories. The overall degree of crystallinity depended significantly on whether the sample was quenched from the melt or whether the sample was annealed in the μ-phase. Samples that were rapidly quenched to 78 K from the melt showed a glass transition, T_g = 139 K. Thus, they were only partially crystallized. Annealing the sample in the μ-phase right above the α_2–μ transition resulted in crystallinities that were near 100%, which was indicated by the lack of a glass transition. The observed fraction of α- or β-polymorphs depended on the rate by which the sample was cooled from the mesophase. Increasing cooling rates resulted in increasing amounts of the α-modification.

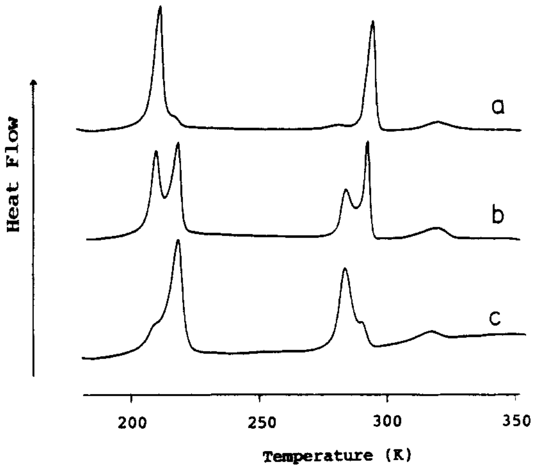


Figure 3. Dependence of variations of the melting of PDES on crystallization conditions, as determined by DSC on heating at 10 K/min: (a) β-polymorph as obtained by annealing at 280 K; (b) DSC trace of PDES after cooling at a rate of 10 K/min; (c) α-rich sample as quenched from the μ-phase to 78 K.

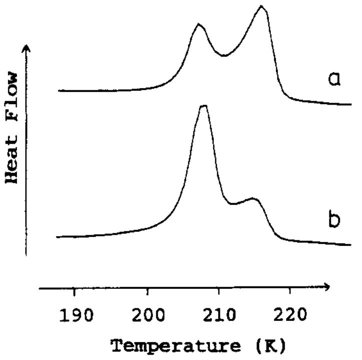


Figure 4. DSC traces of a mixture of α- and β-PDES before (a) and after (b) 300-min annealing at 260 K.

Almost the pure β-modification could be obtained, if the sample was annealed in the temperature range between the α_2–μ and the β_2–μ transition or more conveniently, because of faster nucleation, if the sample was cooled slowly to 265 K and reheated several times to 280 K (Figure 3a). Even by liquid nitrogen cooled butane/propane mixtures, it was not possible to quench the investigated PDES fast enough from the mesophase to get the pure α-modification. The samples always contained small fractions of the β-modification (Figure 3c), the DSC trace of Figure 3b results from a sample cooled at a rate of 10 K/min from the mesophase to 150 K.

The mesophase melts in a rather broad temperature range between about 300 and 320 K. The change in enthalpy at the melt transition, ΔH_μ = 3.1 J/g, is very small compared to that of the α_1–α_2 and α_2–μ as well as the β_1–β_2 and the β_2–μ transitions, e.g., $\Delta H(\beta_1$–$\beta_2)$ = 28 J/g. It contributes only about 3% to the total entropy of fusion, which differs little for the α- and the β-polymorph. Roughly, the changes in entropy observed for the α_1–α_2 and the β_1–β_2 transition are twice as large as the corresponding values of the α_2–μ and the β_2–μ transitions.

Annealing a mixture of the α- and the β-polymorph within the high-temperature phase (α_2/β_2) results in an increase of the heats of transition detected for the β-modification. Figure 4 shows the DSC trace of a mixture of α- and β-PDES before and after annealing the sample for 300 min at 260 K. Obviously, part of the α-PDES were slowly transformed to β-PDES. Thus, the β-modification appears to be thermodynamically more stable than the α-modification, which is also indicated by the higher total entropy of fusion observed on melting the β-modification. It cannot be clarified yet whether the stability of the different polymorphs depends on molecular weight.

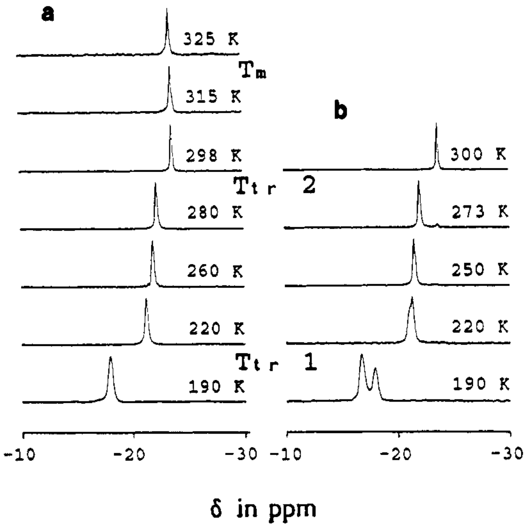


Figure 5. Temperature variation of the MAS ^{29}Si NMR spectrum of poly(diethylsiloxane): (a) spectra of the pure β-modification; (b) spectra of a mixture of a- and b-modification. Spectra were recorded by stepwise heating of the samples and correspond to the DSC traces in parts a and c of Figure 3, respectively.

Solid-State NMR

High-resolution solid-state ^{29}Si NMR spectra of poly(diethylsiloxane) are shown in Figure 5. The temperature-dependent MAS spectra were obtained by heating pure β-PDES (a) and also by heating a mixture of the α- and the β-modification (b).

The β-polymorph gave one sharp signal at −17.9 ppm for the fully ordered crystalline state at 190 K, which did not change on raising the temperature until the β_1–β_2 transition was reached. At the β_1–β_2 transition the resonance was shifted upfield by $\Delta\nu$ = 3.3 ppm to −21.2 ppm. Increasing the temperature further resulted in a gradual upfield shift from −21.2 ppm at 220 K to −22.2 ppm at 280 K, which is directly below the β_2–μ transition. On passing the β_2–μ transition, the isotropic chemical shift of the silicon atoms was shifted to −23.6 ppm. Further heating, even above the melt transition (isotropization), did not result in further variation of the chemical shift. The chemical shift remained the same at 298, 315, and 325 K.

The observed upfield shifts indicate changes in the molecular packing and the bond conformation as the sample is converted from a highly ordered crystal to the isotropic melt. It has been demonstrated that increasing fractions of gauche conformations in polymethylene and poly(dimethylsiloxane) chains can result in upfield shifts of the isotropic solid state ^{13}C and ^{29}Si resonances by several ppm, while changes in the molecular packing result typically in smaller variations of the chemical shifts.[35]

In the isotropic melt, the poly(diethylsiloxane) molecules are coiled. The unperturbed dimensions are similar to those of poly(dimethylsiloxane), which is demonstrated by a characteristic ratio of 7.7.[36] In the melt, the ^{29}Si resonance gives the fast exchange-averaged chemical shift for a dynamic equilibrium between different rotional isomeric states of the Si–O and the Si–C bonds. The fact that the ^{29}Si chemical shift is identical for the melt and the μ-phase demonstrates a dynamically disordered conformational state also below the isotropization transition. This is confirmed by ^{29}Si spin–lattice relaxation experiments. The T_1 time was 23 s for the melt at 330 K and 25 s for the μ-phase at 300 K. Thus, the motional state and the con-

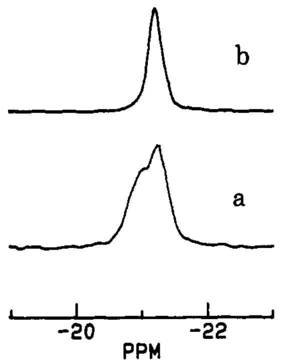


Figure 6. Enlargement of the MAS ^{29}Si NMR resonance of pure β-PDES (b) and a mixture of α- and β-PDES (a), T = 220 K.

formational equilibrium of the molecular segments remain very much the same.

The downfield shift of the ^{29}Si signal on cooling below the μ–β_2 transition may be explained by a change of the segmental conformations *and* the molecular packing. While the density differs only slightly between the melt- and the μ-phase ($\Delta\rho$ = 0.03 g/cm^3), it changes by $\Delta\rho$ = 0.12 g/cm^3 at the μ–β_2 transition.[24] Hence, as the molecules become packed more densely, the conformational interconversion processes will be more and more restricted. The further, continuous shift that is observed when the β_2 sample is cooled demonstrates also the β_2-phase motional averaging between different sites of the ^{29}Si. The resulting dynamic equilibrium changes with decreasing temperature. From the high-resolution ^{29}Si spectra, it cannot be decided whether and to what extend these changes involve rotational isomeric states of the polymer backbone bonds or the side-chain Si–C bonds.

Below the β_1–β_2 transition, the silicon atoms appear to be locked in a single state, which is represented by the −17.6 ppm ^{29}Si resonance. This resonance does not shift even when the temperature is decreased further. Thus, finally, in the β_1-phase, the PDES molecules are packed rigidly in an ordered crystal lattice.

Figure 5b shows the MAS ^{29}Si NMR spectra of a sample that was quenched rapidly from the μ-phase and thus contains both the α- and the β-modification. Two signals could be resolved for the rigid crystal at 190 K. The −16.6 ppm signal was assigned to the α-polymorph while the −17.6 ppm signal is identical with the 190 K ^{29}Si NMR resonance in Figure 5a and represents the β-modification. The fraction of the α_1-modification was calculated to 64% from the signal intensities as the relaxation and cross-polarization behavior of the two modifications did not differ significantly. (See ref 37 for the quantitative evaluation of solid state signal intensities.)

Raising the temperature above the lower disordering transitions resulted in an upfield shift of the ^{29}Si resonances. Up to 220 K, two signals were resolved. This is demonstrated more clearly in the enlargement in Figure 6a. The −20.9 ppm signal can be assigned to the α_2- and the resonance at −21.2 ppm to the β_2-modification by comparison with the corresponding spectrum of Figure 6b. Thus, the α_2- and β_2-modifications are clearly distinguished by the ^{29}Si NMR chemical shifts. The deconvolution of the 220 K resonances yielded only 60% α_2-PDES, which is only little less than the value obtained from the spectrum at 190 K.

When the temperature was raised further, the shoulder disappeared, and only one signal could be resolved. The slow rates for the conversion of α_2- to β_2-PDES as demonstrated by the calorimetric experiments cannot explain this phenomenon. The recording time for the 220 K NMR spectra was 30 min. As described above, annealing the sample for 300 min at 250 K did not result in a complete transformation from α_2- to β_2-PDES. The difference between the α_2- and β_2-PDES are too small to observedly effect the ^{29}Si chemical shift and therefore only one signal resonance is observed.

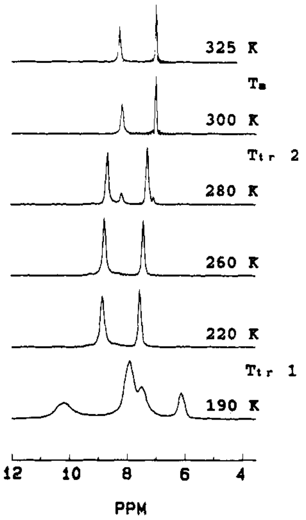


Figure 7. Temperature variation of the MAS ^{13}C NMR spectrum of pure β-PDES corresponding to the DSC trace (a) in Figure 3.

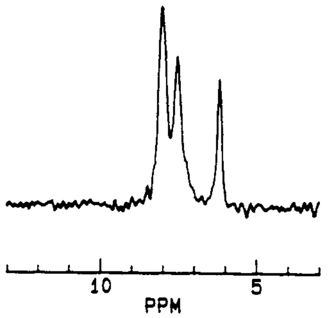
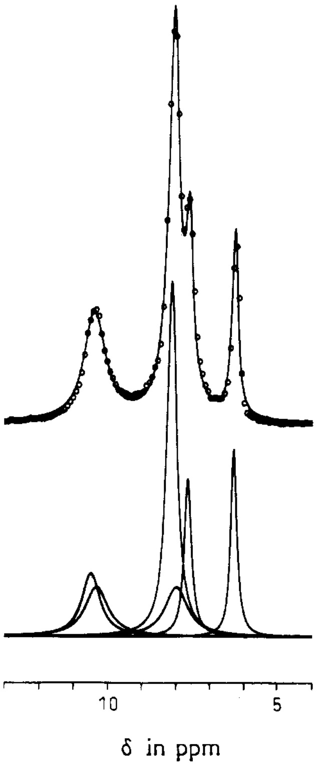


Figure 8. MAS ^{13}C NMR spectrum of β-PDES recorded with a 100-ms delay time between the mixing and the acquisition period. Only the CH_3 signals can be observed.

In the μ-phase, the ^{29}Si NMR shifts recorded for PDES were identical regardless of whether this state was reached upon heating α- or a β-PDES. This was also the case for α-samples that were heated rapidly from low temperatures to the μ-state and whose spectra were recorded immediately, in order to keep the time in which the sample could turn from α_2 to β_2 as short as possible.

MAS ^{13}C NMR spectra of β-PDES at different temperatures are shown in Figure 7. Four signals were clearly resolved at 190 K for β_1-PDES: at 6.2, 7.6, and 8.0 ppm and a broad signal at 10.3 ppm. ^{13}C NMR resonances of methine or methylene carbons can be suppressed in CP spectra if the spectrum is recorded with a delay time after the mixing period.[32] Figure 8 gives a ^{13}C NMR spectrum, which was recorded with a delay time of 100 ms. The remaining resonances at 8.0, 7.6, and 6.2 ppm were assigned to the CH_3 groups.

Deconvolution in Lorentzians is shown in Figure 9. The spectrum was fitted by six lines, one of which is three times as intense as the others: 10.4 ppm (1), 10.25 ppm (1), 8.1 ppm (1), 7.95 ppm (3), 7.6 ppm (1), and 6.2 ppm (1). The numbers in parenthesis give the relative intensities. X-ray experiments showed two $Si(CH_2CH_3)_2O$ segments in the unity period.[24] Thus, each of the single-intensity signals can be assigned to one of the eight carbons in the unit cell and the 7.95 ppm signal represents the remaining three



ppm	Rel. Int.	Δν 1/2 (Hz)
10.4	0.125	47
10.25	0.125	80
7.95	0.125	60
8.1	0.375	25
7.6	0.125	19
6.2	0.125	16

Figure 9. Deconvolution of the 190 K ^{13}C NMR spectrum of β-PDES: top, fit of the calculated (—) to the experimental (○) spectrum; bottom, plot of the deconvoluted Lorentzians, the insert gives the fitting parameters.

carbons whose signals overlap in an unresolavable way. Comparison to the spectrum in Figure 8 shows that the signal at 8.0 ppm in the experimental spectrum results from the overlapping resonances of methylene and methyl carbons. The deconvolution into two lines at 8.1 and 7.95 ppm with an intensity ratio of 1:3 is in agreement with an overlap of two methylene and two methyl carbon signals. Thus, the ^{13}C NMR spectrum is in agreement with the X-ray data. The four CH_2 groups of the identity unit may be assigned to the 10.4, 10.25, and 8.1 ppm signals and part of the 7.95 ppm signal and correspondingly the four CH_3 groups to the 7.6 and 6.2 ppm signals and also part of the 7.95 ppm signal.

The fact that the ^{29}Si spectrum showed only one sharp resonance might be attributed to a lower sensitivity of the Si atoms to intermolecular variations, because they are located in the core of the chain molecules.

Raising the temperature above the β_1–β_2 transition resulted in a collapse of the CH_3 and CH_2 splittings. Two ^{13}C NMR signals were observed for β_i-PDES of which the 8.8 ppm resonance was assigned to methylene carbons and the 7.5 ppm signal to methyl carbons. Because the X-ray experiments did not show a change of the crystal lattice and of the unity period[24] at the lower solid–solid transition of β-PDES, the collapse of the splittings has to be explained by the onset of molecular motions in the side chain, which equalize the differences between the ethyl groups.

In contrast to the ^{29}Si signals, the MAS ^{13}C NMR spectra for the β_2-modification did not change significantly on raising the temperature up to the β_2–μ transition. Signals shift from 8.8 and 7.5 ppm at 220 K to 8.6 and 7.3 ppm at 280 K. In the spectrum at 280 K, the signals of the μ-phase can already be observed.

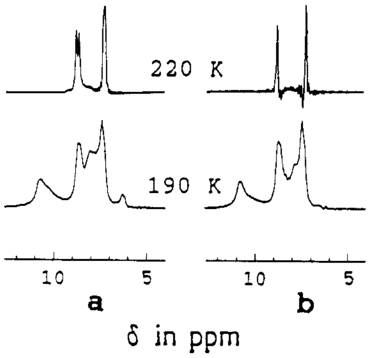


Figure 10. MAS ^{13}C NMR spectrum of a mixture of α- and β-PDES below and above the low-temperature disordering transition (a) in comparison to the spectrum of pure α-PDES and (b) as obtained by subtraction of the corresponding β-resonances shown in Figure 6.

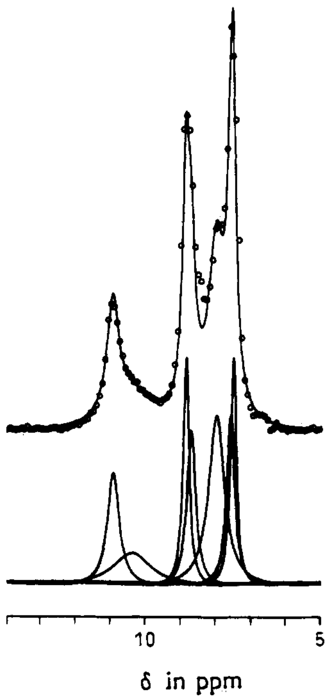
At the transition to the μ-phase the CH_2 and the CH_3 signal are shifted further upfield to 8.2 and 7.06 ppm as recorded at 300 K. An additional small shift of the CH_2 signal to 8.35 ppm at 325 K is observed at the transition to the isotropic melt.

Similar observations as described above were made for the ^{13}C spectra of α-PDES. Figure 10a presents the ^{13}C NMR resonances below and above the lower solid–solid transition for a sample that contains both polymorphs. The spectra in Figure 10b were obtained by subtraction of the corresponding spectrum of pure β-PDES. They thus represent the pure α-modification. Deconvolution of the 190 K spectrum of Figure 10b is shown in Figure 11. Six signals of equal intensity and one signal with twice this intensity resulted: 10.8 (1), 10.3 (1), 8.8 (1), 8.65 (1), 7.95 (2), 7.55 (1), 7.5 (1) ppm. The numbers in parentheses give the relative intensities. Also in this case, the ^{13}C NMR spectrum of α-PDES can be explained by partial overlapping of four methylene and four methyl carbon resonance and is consistent with X-ray data,[24] which demonstrate two monomer units per unit cell.

Above the α_1–α_2 transition, the ^{13}C NMR spectrum collapsed to four signals. Consistent with the 220 K ^{29}Si spectra, the comparison with the carbon spectrum of β-PDES demonstrated that the fine splitting is due to the coexistence of α- and β-PDES (Figure 12). The deconvolution shown in Figure 13 gave four signals at 8.9, 8.8, 7.5, and 7.4 ppm, from which the 8.9 ppm and the 7.4 ppm resonance were assigned to the CH_2 and the CH_3 carbons of α-PDES. An additional broad line at 8.35 ppm with a relative intensity of about 10% was necessary to fit the spectrum. This signal may be due to an amorphous fraction, which could not crystallize on quenching the material. Raising the temperature, the difference between the α_2 and the β_2 signals decreases. At 260 K, the signals are only slightly broadened, corresponding to the results from ^{29}Si NMR.

In order to obtain complementary information about the motional state of the chain segments, we recorded the chemical shift anistropies (CSA) of the silicon and the carbon nuclei. Figure 14 presents the ^{29}Si NMR of β-PDES as obtained without magic angle sample spinning.[38] The sample was crystallized as described above, MAS ^{29}Si NMR spectra did not show any detectable fraction of the α-polymorph.

An axially symmetric spectrum with a total line width of 3.1 kHz ($\nu_z - \nu_x$) was obtained at 110 K. The shape and width of the spectrum reflect the powder distribution of



ppm	Rel.Int.	Δν 1/2 (Hz)
10.8	0.125	30
10.3	0.125	100
8.8	0.125	16
8.65	0.125	22
7.95	0.250	40
7.55	0.125	20
7.5	0.125	15

Figure 11. Deconvolution of the 190 K ^{13}C NMR spectrum α-PDES from Figure 10b: top, fit of the calculated (—) to experimental (O) spectrum; bottom, plot of the deconvoluted Lorentzians, the insert gives the fitting parameters.

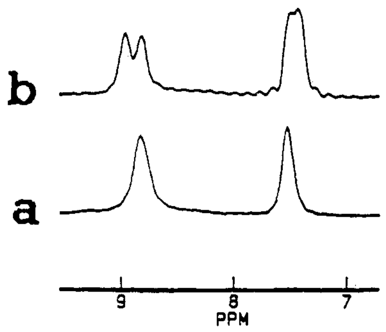
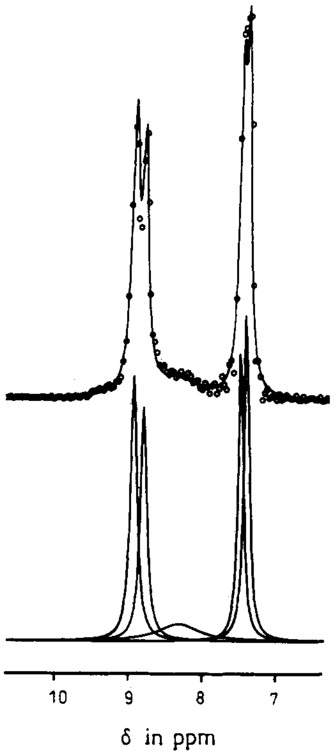


Figure 12. Comparison of the enlarged MAS ^{13}C NMR spectra of pure β-PDES (a) and a mixture of α- and β-PDES (b) at T = 220 K.

the crystallites without motional averaging. On heating, the signal did not change until the lower solid–solid transition was reached. Above the transition to the high-temperature phase, the line width was slightly reduced to 2.6 kHz, while the shape remained almost axially symmetric. The slight narrowing indicates the onset of fast molecular motion, which, however, is of little amplitude. When the temperature was raised further, it became more obvious that the ^{29}Si CSA deviates from axial symmetry. This indicates slight changes of the motional state within the high-temperature phase corresponding to the significant shift of the isotropic ^{29}Si resonance in this temperature range.

The spectrum at 280 K resulted from a superposition of the resonances of the high-temperature phase and the μ-phase. No isotropic components could be detected by cross-polarization experiments.



ppm	Rel.Int.	Δν 1/2 (Hz)
8.9	0.24	8.0
8.8	0.21	8.0
7.5	0.21	6.5
7.4	0.24	6.5
8.35	0.10	50.0

Figure 13. Deconvolution of the ^{13}C NMR spectrum of α- and β-PDES at 220 K: top, fit of the calculated (—) to experimental (O) spectrum; bottom, plot of the deconvoluted Lorentzians, the insert gives the fitting parameters.

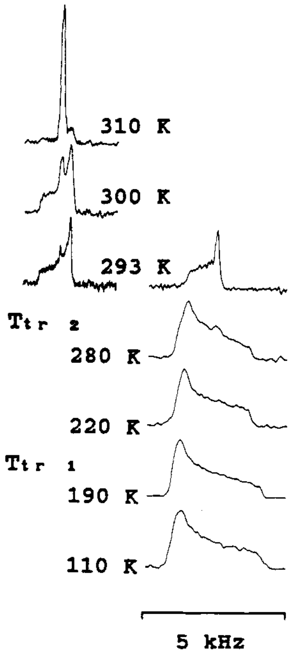


Figure 14. Temperature dependence of the ^{29}Si chemical shift anisotropy (high-power decoupled ^{29}Si NMR without MAS) as recorded on stepwise heating of pure β-PDES: right column, CP spectra; left column, single-pulse excitation.

Significant narrowing of the line width from 2.6 kHz at 280 K to 1.1 kHz at 293 K was observed on raising the temperature above the β_2–μ transition. The 293 K spectrum gives evidence of the onset of anisotropic, large-amplitude, motional processes. The correlation time of the molecular motion is less than 3×10^4 s, according to the time scale of the ^{29}Si NMR experiment. The axial symmetry of the motionally averaged CSA is explained by diffusive or jump-type rotational motion of the chain segments. In case of a macromolecule, the axis of such rotational motion should coincide with the chain axis. As the MAS ^{29}Si NMR spectra indicated similar conformational disorder in the mesophase and in the melt, the molecular mobility in the mesophase may be described by fast conformational reorientations of the segments around the molecular long axis.

^{29}Si CSA spectra that were recorded without cross polarization are shown in the left column of Figure 14. The observed spectra represent a superposition of the anisotropically averaged 1.1-kHz spectrum and an isotropically averaged component with 100-Hz line width. Above the α_2–μ and β_2–μ transitions, the sample consists obviously of isotropic and anisotropic components. The relative fraction of the anisotropic component is decreasing continuously, when the temperature is increased. This corresponds to the very broad transition to the isotropic melt as observed in DSC experiments. Yet, it cannot be decided whether the broadness indicates a non-first-order transition or whether it may be explained by the broad molecular weight distribution. Recent data reported by Godovsky and Papkov[25] showed a remarkable dependence of the isotropization transition on molecular weight.

Only the sharp signal of 100-Hz line width could be observed above 322 K. Isotropic molecular reorientation in the melt results in the sharp isotropic chemical shift signal.

The ^{29}Si chemical shift anisotropies of a sample that was predominantly α-PDES did not differ from those reported for the β-modification. The resonance appeared only slightly broader below the lower solid–solid transition. However, this broadening has its origin in the overlap of the CSA of α-PDES and the slightly shifted signal to β-PDES.

Temperature-dependent, high-power, ^{1}H-decoupled ^{13}C NMR spectra that were recorded without magic angle sample spinning are shown in Figure 15. No defined line shape of the chemical shift anisotropy could be observed for the ^{13}C nulcei. The recorded signals are superpositions of the chemical shift anisotropies for the different chemical sites of the ^{13}C atoms. Slight narrowing of the total line width from about 1.7 kHz at 100 K to about 1.1 kHz at 190 K (as determined at the bottom of the signal) demonstrates the occurrence of reorientational processes of the ethyl side chains already in the β_1-phase. The conversion to the β_2-modification results in a further decrease of the line width from 1.1 kHz at 190 K to about 1 kHz at 220 K. This indicates a cooperative onset of additional motional processes, which explain the coalescence of the MAS ^{13}C NMR spectra discussed above.

A continuous decrease of the line width to about 800 Hz at 280 K on raising the temperature further shows a continuous increase of the side-chain mobility.

While the chemical shift anisotropy of the silicon atoms decreased sharply at the transition to the μ-phase, no step-type narrowing of the ^{13}C resonance occurred at the transitions to the μ-phase and on isotropization. However, the gradual decrease of the line width continued until finally the CH_2 and the CH_3 carbon signals could be separated when the sample was molten.

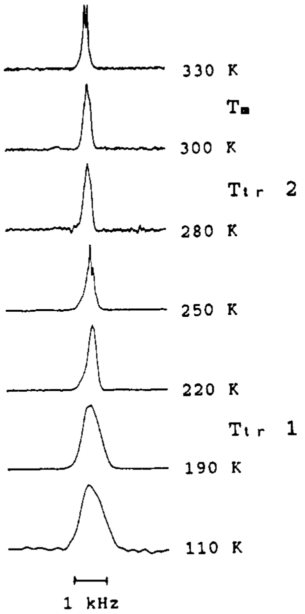


Figure 15. Temperature dependence of the ^{13}C chemical shift anisotropy (high-power decoupled ^{13}C NMR without MAS) as recorded on stepwise heating of pure β-PDES.

Conclusion

The variable-temperature ^{29}Si and ^{13}C NMR experiments allow correlation of the onset of molecular motion and structural disordering with the different transitions that can be observed by thermal analysis. The α- and β-modifications of poly(diethylsiloxane) are distinguished in the high-resolution ^{29}Si as well as in the ^{13}C NMR spectra. DSC experiments on annealed samples demonstrated β-PDES as the thermodynamically more stable modification. The slow conversion is in agreement with a highly restricted motion of the polymer chains above the lower disordering transition as observed by the NMR experiments. While in the NMR experiments the two modifications became indistinguishable already 50 K below the second solid–solid transition, the DSC experiments discriminated the different polymorphs even when the sample was annealed for extended times directly below the upper disordering transition. As far as the NMR spectra allow a discrimination between α- and β-PDES, there is a difference in the molecular structure but not in the molecular dynamics.

Comparison of ^{29}Si and ^{13}C NMR spectra allows the separation of disordering and the motion of the polymer backbone and the side chains. Motional processes that involve the side chains were indicated already below the α_1- or the β_1-transition by a partial averaging of the ^{13}C CSA. As the isotropic chemical shifts and the crystal packing were not effected, no disordering is indicated. Thus, the effects may be explained by jump-type motions of the ethyl groups. No motion of the backbone, which would result in narrowing of the ^{29}Si CSA, could be observed below the lower solid–solid transition.

A considerable upfield shift of the isotropic ^{29}Si signal but only a slight reduction of the ^{29}Si CSA from 3.1 to 2.6 kHz demonstrates a change in the conformation of the backbone at the lower transition, which is accompanied by low-amplitude motional narrowing. This agrees with Raman experiments,[27] which indicated the onset of conformational disordering and molecular mobility of the –SiO– backbone at the lower transition. Fast jump-type changes of the oriention of the Si–O–Si plane over only small angles would strongly influence the dielectrical properties and thus the Raman results, even when the amplitudes of the motion are small. However, it would effect the chemical shift anisotropy only little as it was observed by the NMR experiments. In contrast, X-ray data did not detect considerable changes in the powder pattern.

The coalescence of the MAS ^{13}C signals and the significant narrowing of the ^{13}C CSA from 1.1 to about 1 kHz show the onset of additional side-chain motion. It is concluded that the molecular motion that starts at the first transition concerns mainly the side chains, while the mobility of the backbone is still strongly restricted. Thus, the claim from Raman data that the side chains do not participate in the molecular motion cannot be confirmed.[27] The Raman spectra are not sensitive to the side-chain motion.

The already reduced ^{13}C CSA is little effected at the transitions to the μ-phase (α_2–μ and β_2–μ), while the still broad ^{29}Si CSA was significantly narrowed. Meltlike conformational disordering in the mesophase is indicated by the absence of an additional shift of the isotropic ^{29}Si resonance at the transition from the mesophase to the melt. The molecular motion, which starts at the α_2–μ and the β_2–μ transition, may be described by conformational interconversion processes, which allow diffusive rotation of $Si(CH_2CH_3)_2$ segments. Thus, the axial symmetry of the ^{29}Si CSA is explained. However, because the molecules are still packed in a monoclinic lattice,[24] it appears that the motion is not fully axially isotropic. As the ^{29}Si nuclei are shielded by the ethyl side groups, their isotropic chemical shift and their CSA are not effected by small changes in the averaged intermolecular arrangement.

Note Added in Proof. While this paper was in press, we got a notice of related ^{29}Si NMR investigations with results which are consistent with ours: Litvinov, V. M.; Whittaker, A. K.; Hagemeyer, A.; Spiess, H. W. *Colloid & Polymer Science*, in press.

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Registry No. PDES (homopolymer), 88483-06-1; PDES (SRU), 28323-47-9.

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