Mesomorphism, molecular structure and dynamics of polydiethyilsiloxane

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The correlation between the phase behaviour of polydiethyilsiloxane (PDES) and conformational and motional changes at the various disordering transitions has been investigated by nuclear magnetic resonance (n.m.r.), dielectric relaxation and shear experiments. Diffusive rotation of the chain segments around the long axis of the molecules is indicated by $^{29}$Si n.m.r., below the isotropization transition. The remarkably fluid character is explained in part by the coexistence of anisotropic and isotropic motional states of the $\text{-OSiEt}_2\text{-}$ segments, which indicate microscopic domain formation. The molecular motion in the $\alpha_2$- and $\beta_2$-phases is restricted but still fast with respect to the $^{29}$Si n.m.r. timescale. Transmission electron micrographs show, besides chain-folded lamellae, also extended-chain lamellae. These differences in the morphologies can explain why the interconversion of $\alpha_2$-PDES into the thermodynamically more stable $\beta_2$-polymorph is slow, in spite of the pronounced mobility of the polymer segments. Long-range reorganization processes have to be considered to allow the morphological changes observed by electron microscopy.

(Keywords: mesomorphism; molecular structure; dynamics; polydiethyilsiloxane)

INTRODUCTION

High-molecular-weight polydiethyilsiloxane exists in two crystalline polymorphs, $\alpha$- and $\beta$-PDES. Each of them undergoes a disordering transition from $\alpha_1$ to $\alpha_2$ and from $\beta_1$ to $\beta_2$ respectively.1-13. Annealing experiments allowed us to identify the $\beta$-modification as the thermodynamically stable one. Both polymorphs convert prior to isotropization into a phase $\mu$, which is also referred to as the $\alpha_\mu$-phase.3,4. The observed fractions of $\alpha$- or $\beta$-polymorph depend on the rate at which the sample is cooled from the $\mu$-phase. Increasing cooling rates result in increasing amounts of the $\alpha$-modification. The $\alpha_2-\mu$ transition occurs at 280 K, the $\beta_2-\mu$ transition at 290 K. The $\mu$-phase melts in a rather broad temperature range between about 300 and 320 K. The change in enthalpy at the isotropization transition is small compared to that of the $\alpha_1-\alpha_2$ and $\alpha_2-\mu$ as well as the $\beta_1-\beta_2$ and $\beta_2-\mu$ transitions. It contributes only about 3% to the total entropy of fusion, which differs little for the $\alpha$- and the $\beta$-polymorph.6-9. The formation of the $\mu$-phase has not been observed for low-molecular-weight fractions of PDES, which contained large amounts of cycles.8,10. N.m.r. and Raman experiments showed the onset of molecular motion at the various solid-solid transitions, which results in dynamic conformational disordering. In the present paper, we discuss morphological differences and solid-state properties of $\alpha_2$, $\beta_2$- and $\mu$-PDES in relation to the molecular structure and dynamics.

EXPERIMENTAL

Materials

Sample preparation and characterization (gel permeation chromatography, osmosis and thermal analysis) have been described before. The investigated sample had a number-average molecular weight of 93 000 as obtained from osmotic pressure experiments. Gel permeation chromatography according to a calibration by standard polystyrenes gave molecular weights of $M_n = 50 000$ and $M_w = 83 000$.

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

Methods

D.s.c. measurements were performed on a Perkin-Elmer DSC 7. 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$^{-1}$. Typically, the sample weight was chosen between 0.5 and 1 mg. Temperature accuracy was better than $\pm 1$ K. The onset of the recorded endotherm on heating is given for the transition temperatures. Transition entropies were calculated assuming equilibrium, i.e. $T_m \Delta S_m = \Delta H_m$.

Solid state $^{29}$Si and $^{13}$C n.m.r. spectra were recorded on a Bruker CXP 300 spectrometer at 59.63 MHz and 75.47 MHz respectively. A Bruker double-bearing magi-
angle spinning (MAS) probe, which was modified for variable-temperature experiments, was used. Two different pulse sequences were used to generate the spectra. The usual spin-lock cross-polarization (CP) sequence\textsuperscript{14} was applied for the spectra in the low- and the high-temperature phase. In this case, a 90° pulse (3.9 μs for \textsuperscript{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 being applied. Delay times between 10 and 600 s were chosen, to be at least five times as long as \( T_1 \) to ensure complete relaxation between each pulse experiment. Temperatures were measured by means of a thermocouple adjacent to the rotor with an accuracy of ± 3 K.

Spin–lattice relaxation times of PDES in the \( \mu \)-phase and in the melt were measured by means of an inversion recovery pulse sequence. A 180° pulse was followed by a variable delay time before acquisition. To determine \( T_1 \) of \( \alpha \)- and \( \beta \)-PDES, an additional 90° pulse was employed after the cross-polarization sequence, which resulted in a \( z \) orientation of the magnetization. After a variable delay for relaxation, a simple 90° pulse was employed to allow acquisition.

Electron micrographs were obtained on a Zeiss EM 902 with an acceleration voltage of 80 kV. One-stage carbon replicas were prepared from freshly fractured surfaces at 170 K with a "Gefrier/itzanlage Balzer BAF". The specimens were shaded with platinum under rotation at an angle of 30° or without rotation under an angle of 45°. Dielectric relaxation was measured with a Hewlett-Packard Impedance Analyzer HP 4192 with a frequency of 10,000 Hz. Two gold-coated quartz plates with a spacer of 75 μm width were used as condenser plates.

Birefringence micrographs were obtained by means of a polarization microscope (Leitz Ortholux II Pol BK) with a hot stage (Mettler FP52).

Creep recovery experiments were carried out with a Rheometrics Stress Rheometer, RSR. A 25 mm cone-and-plate fixture with a cone angle of 0.1 rad was used. A constant torque was employed long enough to observe constant shear rates. Extrapolation of the steady shear viscosities thus obtained yielded the \( \eta_0 \) values. Temperature control was achieved by means of a thermostated liquid bath with a constancy of ± 0.5°C.

RESULTS

Recently we reported solid-state \(^{13}\)C and \(^{29}\)Si n.m.r. data on PDES and discussed them in comparison with the thermal behaviour\textsuperscript{8}. Changes of the isotropic \(^{29}\)Si resonance at the solid–solid transitions (\( \chi_1-\chi_2 \), \( \beta_1-\beta_2 \), \( \chi_2-\mu \) and \( \beta_2-\mu \)) indicate dynamic disordering of the conformation of the polymer backbone. The two polymorphs \( \chi_1 \) and \( \beta_1 \) can be clearly distinguished by their isotropic \(^{29}\)Si and \(^{13}\)C resonances. A considerable upfield shift of the isotropic \(^{29}\)Si resonance line demonstrates a change of the polymer backbone conformation. Only small differences are observed for \( \chi_2 \)- and \( \beta_2 \)-PDES in the isotropic \(^{29}\)Si n.m.r. chemical shifts, and the two modifications become indistinguishable already 50 K below the transition to the \( \mu \)-phase. The corresponding difference in the \(^{13}\)C spectra is slightly larger and can be observed even 20 K below the upper disordering transition. The results demonstrate nearly identical conformations of the two polymorphs in their high-temperature phase. Liquid-like disordering is indicated for the \( \mu \)-phase by the \(^{13}\)C and \(^{29}\)Si chemical shifts, which are the same as those of the isotropic melt.

Variations in the motional state of PDES segments are also indicated by spin–lattice relaxation experiments. The \( T_1 \) times showed significant changes, which are consistent with the onset of different motional processes discussed above. Corresponding to the \( \beta_1-\beta_2 \) transition, \(^{29}\)Si \( T_1 \) drops sharply from 200 s at 180 K and 270 s to 30 s at 220 K. Within the \( \beta_2 \)-state, \( T_1 \) increases to 52 s at 250 K and 80 s at 270 K. An additional significant decrease of the \( T_1 \) time is observed at the transition to the \( \mu \)-phase: \( T_1 \) drops to 25 s at 300 K, 20 s at 315 K and 23 s at 330 K. Upon isotropization, no further change of the \( T_1 \) times is observed within the experimental error.

The results are in agreement with Raman\textsuperscript{7} and \(^{1}\)H n.m.r.\textsuperscript{11,12} experiments, which indicated the onset of side-chain motion and low-amplitude –Si–O– segment torsion at the lower disordering transition. Litvinov et al. gave a detailed picture of the segmental motions and the corresponding frequencies based on their very careful \(^{1}\)H n.m.r. second moment and relaxation experiments\textsuperscript{11,12}. This is the onset of side-chain mobility and torsional vibrations of the Si–O links upon the lower disordering transition and polymer backbone reorientation above the second disordering transition.

Nuclear magnetic resonance

The motional states of the PDES molecules can be observed directly by the \(^{29}\)Si chemical-shift anisotropies (CSA). This is shown in Figure 1 for \( \beta \)-PDES. No differences could be observed on recording the CSA of a sample that consisted mainly of \( \alpha \)-PDES. The \(^{29}\)Si CSA is not significantly motionally narrowed below the lower solid transition. The spectrum is almost axially symmetric, with \( \nu_x-\nu_z=3.1 \) kHz. In contrast, motional narrowing is observed for the \(^{13}\)C CSA already below the lower disordering transition. The total linewidth for the CH\(_3\) and the CH\(_2\) carbons changed from about 1.7 kHz at 100 K to 1.1 kHz at 190 K. Thus, side-chain mobility is observed below the lower disordering transition, while the polymer backbone remains fixed on the n.m.r. timescale.

The \(^{29}\)Si CSA becomes slightly narrowed and remains almost axially symmetric when the temperature is raised above the lower transition, \( \nu_x-\nu_z=2.9 \) kHz. This can be explained by the onset of small-amplitude –Si–O–backbone motions. The deviation from axial symmetry becomes more pronounced with increasing temperature. A non-axially symmetric spectrum with \( \eta=0.14 \) and \( \nu_x-\nu_z=2.6 \) kHz was recorded at 280 K. This indicates increasing amplitudes of the molecular motion. No significant difference between the spectra of \( \beta_2 \) and \( \chi_2 \)-PDES could be observed.

Additional narrowing of the \(^{29}\)Si CSA from 2.6 kHz to 1.1 kHz at the transitions to the \( \mu \)-phase reveals the onset of large-amplitude molecular mobility of the backbone. The spectrum at 293 K is again axially symmetric with \( \nu_x-\nu_z=1.1 \) kHz and \( \eta=0.0 \). The axial symmetry indicates diffusive averaging around the \( z' \) axis of the CSA, which may be explained by a diffusive rotational motion of the chain segments around the long axis of the molecules\textsuperscript{8}. Motional decoupling of chain...
segments in an as-yet unknown length is allowed by liquid-like conformational interconversion as indicated by the isotropic chemical shift. Such rotational and translational disordering was already postulated by Papkov, Godovsky et al. from the sharp decrease in the X-ray intensity with 203,4.

Similar CSA 29Si n.m.r. experiments on PDES were performed by Litvinov, Spiess et al. parallel to this work. They attempted a more quantitative interpretation of the 29Si CSA for α2- and β2-PDES. Assuming that the z-axis of the 29Si CSA is perpendicular to the chain axis, they showed that backbone oscillation with an angle not over 40° can be responsible for the line narrowing and the deviation from axial symmetry.

The lineshapes of the spectra at 280 K and at higher temperatures do not represent simple CSA patterns. From comparison of the different spectra, it is obvious that they represent superpositions of the resonances for different PDES modifications. Special care was taken to analyse these superpositions and to separate the effects from non-axial motional narrowing.

The right column in Figure 1 shows 29Si CSA spectra that were recorded by a single 90° pulse excitation in combination with high-power decoupling and a sufficient delay to ensure complete relaxation of all modifications. The spectrum in the μ-phase clearly consists of the anisotropically averaged μ-phase signal with a width of 1.1 kHz and an isotropically averaged part with a linewidth of about 100 Hz. The fraction of the isotropic portion grows with increasing temperature.

Also the CP spectrum at 280 K in Figure 1 represents a superposition of different signals. Figure 2a presents the CSA of PDES at 280 K, which was recorded without cross-polarization and a sufficient delay to ensure complete relaxation of all modifications. The sample was rapidly cooled from room temperature to 180 K and then warmed to 280 K. Thus, it consists of β- and α-PDES. The main, broad component can be assigned to α2- or β2-PDES by comparison with spectra recorded at lower temperatures. Also a small isotropically averaged fraction is evident. In contrast, no isotropic component could be observed in cross-polarization experiments.

The components could be separated by means of an inversion recovery experiment15, due to the significant difference in 29Si T1 relaxation times. A 180° pulse was followed by a delay time T1(β2)>r>T1(μ). The free induction decay (FID) was recorded after an additional 90° pulse. The 180° pulse turned the magnetization into the −z direction. The slowly relaxing component did not change within the delay time, while components with short T1 relaxed back into the +z direction. The following 90° pulse generated an FID that transformed to a negative signal of the slowly relaxing component and a positive signal of the fast relaxing component.

Figure 2b shows a spectrum that was recorded with a delay time of τ = 25 s. For convenience, the spectrum was inverted by a 180° phase correction, so that signals that correspond to slow T1 times are shown positively. The signal is a superposition of the hardly relaxed broad component, which is observed as a positive signal, and the negative signal of the fully relaxed narrow component. Addition of the two spectra results in the spectrum in Figure 2c, which is a one-component non-axially symmetric CSA with ν = 2.6 kHz and η = 0.14. This spectrum represents the CSA of α2- and β2-PDES without the superimposed narrow component. Figure 2d resulted when the spectrum of Figure 2b was subtracted from that in Figure 2a. The signal consists only of the narrowed component with short relaxation time. Comparison with the spectra above Ttr 2 reveals that the spectrum represents a portion of the sample that has already transformed into the μ-phase and, in addition, an isotropic component. The isotropic component indicates an amorphous fraction.

![Figure 1](image_url) Temperature variation of the 29Si chemical-shift anisotropy of a β-PDES as recorded with cross-polarization (right column) and by single-pulse excitation without cross-polarization (left column).

![Figure 2](image_url) 29Si CSA of a mixture of α2- and β2-PDES: (a) recorded at 280 K without cross-polarization; (b) recorded by means of an inversion recovery experiment, τ = 25 s, the spectrum is 180° phase corrected; (c) spectrum as obtained by addition of spectra (a) and (b); (d) spectrum as obtained by subtraction of spectrum (b) from spectrum (a).
The sample was quenched from 300 K, where already a significant part of the sample showed an isotropic mobility in the $^{29}$Si CSA. In contrast, careful cooling of PDES within the $\mu$-phase resulted in an increase of the crystallinity to almost 100%, as shown by the 293 K spectrum in Figure 1.

Dielectric relaxation

The slight narrowing of the $^{29}$Si CSA on raising the temperature above the $x_1$-$x_2$, respectively $\beta_1$-$\beta_2$, transition was explained by the onset of –Si–O– librations. Such a reorientation of the Si–O segments affects the dielectric properties of PDES due to the considerable dipole moment of the Si–O bond ($q = 0.6 \text{ D}$)\(^1\). Figure 3 presents the temperature dependence of the apparent dielectric constant $\epsilon_r$, which was recorded for PDES at a frequency of 10 kHz. No significant frequency dependence was observed between 100 Hz and 100 kHz at the investigated temperatures. Varying the temperature, an increase of $\epsilon_r$ was observed at the lower transition. The increase of $\epsilon_r$ at the upper transition can be explained by the decrease of the density of the sample (12%) and thus a decrease of the orienting dipoles per volume. No additional increase of the main-chain mobility is observable by dielectric relaxation at the $\beta_2$-$\mu$ transition and at the isotropization temperature.

Microscopy

On annealing, $x_2$-PDES converts into the thermodynamically more stable $\beta_2$-PDES. We observed about 50% conversion within 6 h at 260 K for a sample that consisted predominantly of $x_2$-PDES. Molecular packings in both crystal modifications are similar, and even become indistinguishable by high-resolution solid-state n.m.r. experiments. In view of the high molecular mobility, which is observed by $^{13}$C n.m.r. $^{29}$Si n.m.r., dielectric relaxation and also Raman spectroscopy\(^7\), rearrangement on small scales should occur almost instantaneously. Thus, the slow conversion of $x_2$-PDES into $\beta_2$-PDES indicates that long-range molecular motion with long correlation times is necessary to transform $x_2$ into $\beta_2$-PDES. This implies differences in the crystallite morphology. The question was studied by transmission electron microscopy on replicas of PDES fracture surfaces. The $x_2$- and $\beta_2$-PDES samples were prepared by the procedures described before, and afterwards cooled rapidly to $-150^\circ\text{C}$. Surface replicas were prepared from freshly broken samples by vacuum coating with carbon/platinum. The replicas of the deep-frozen samples represent the crystallite morphologies of the corresponding PDES modification.

Figure 4 shows micrographs that were obtained for $x$- and $\beta$-PDES. Figure 4a represents a replica of a $\beta$-PDES sample. The orientation of the fracture surface was perpendicular to the steel support on which the sample was crystallized in the careful annealing process necessary to obtain pure $\beta$-PDES. Crystallite layers of 2000–5000 Å enclose a triangle with a flat non-regular structure in the centre of the photograph. This might represent the surface of a lamella whose orientation is parallel to the image plane. The most important point appears to be the thickness of the lamellae, which indicates the formation of extended-chain crystals. Comparison with pictures of chain-folded and anabaric polylethylene samples\(^8,\)\(^9\) shows a great similarity to the morphology of extended-chain polyethylene crystals.

Almost unstructured images as shown in Figure 4b resulted when a $\beta$-PDES sample was broken parallel to the support on which the sample was annealed. Probably, only lamellae surfaces are observed. As the specimen had a thickness of more than 1 mm, this demonstrates strong orientation of the crystal axis by the support surface during annealing in the mesomorphic state.

A significantly different morphology was observed for fracture surface replicas of $x$-PDES as shown in Figure 4c. Lamellae with a thickness of about 300–600 Å can be observed. This is in agreement with SAXS data, which showed long periods of corresponding length, and gives evidence for a chain-folded crystal morphology in the case of $x$-PDES.

A replica of a sample that contains both polymorphs is shown in Figure 4d. Besides thin lamellae with a thickness of about 500 Å on the left of the picture, large flat crystal faces can be observed, which are up to 8000 Å and are separated by softly bent depressions.

In summary, the electron micrographs demonstrated lamellar crystallization in case of $x$-PDES and extended-chain crystallization in the case of $\beta$-PDES. We could not observe thin lamellae in $\beta$-PDES samples. Extended crystal faces in $x$-PDES samples might be assigned to domains of $\beta$-PDES, as known that the $x$-PDES samples practically always contain some $\beta$-PDES.

In the highly disordered but still anisotropic $\mu$-phase, the liquid-like segment mobility is large enough that the samples can easily flow. Figure 5a presents optical micrographs of PDES under crossed polarizers. As reported also before\(^6\), the sample is birefringent and distinct crystallites can be observed. Figure 5b presents the micrographs after shearing at 300 K. The distinct crystallites disappeared and the birefringence became uniform, which indicates that the sample was oriented by shearing.

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**Figure 3** Temperature dependence of the dielectric constant $\epsilon_r$ of pure \(\beta\)-PDES

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POLYMER, 1990, Vol 31, August 1541
Viscoelasticity

To investigate changes in the viscoelasticity upon the transition from the isotropic state to the $\mu$-phase, we performed simple shear and also creep recovery experiments. A constant stress ($\sigma$) was applied to shear the sample and the resulting deformation ($\gamma$) was measured as a function of the time by means of a cone-and-plate fixture. Figure 6a presents a creep recovery experiment at 300 K in which a stress of $\sigma_0 = 3000 \text{ N m}^{-2} \text{ K}^{-1}$ was applied. At this temperature, the sample is in the $\mu$-state. The material showed a viscoelastic behaviour, and the recoverable compliance $J_r(t \to \infty) = 8 \times 10^{-5} \text{ m}^2 \text{ N}^{-1}$ was (within experimental error) equal to the compliance calculated from the intercept of the steady-state shearing, $J_r(t \to 0) = 6.5 \times 10^{-5} \text{ m}^2 \text{ N}^{-1}$. An apparent viscosity of $\eta = 9 \times 10^7 \text{ N s m}^{-2}$ resulted after about 2 h according to the relation $\eta = \sigma_0 / \gamma$. (It must be noted that the viscosity is no longer scalar because of the anisotropy in the $\mu$-phase.) Figure 6b represents the same creep recovery experiment with a much longer shearing time. Considerable shear thinning occurred after about 5 h. The apparent viscosity decreased from $6.5 \times 10^7 \text{ N s m}^{-2}$ after 2 h to $1.6 \times 10^7 \text{ N s m}^{-2}$; however, the value remained larger than the melt viscosity. Figure 7 represents the temperature dependence of the steady-state viscosity. The viscosity dropped by five orders of magnitude when the temperature was raised above the isotropization transition and the flow behaviour became Newtonian. No shear-rate dependence was observed even for the highest applied stress ($36000 \text{ N m}^{-2}$). Below the transition to the $\alpha$- or $\beta$-phase, the viscosity was too high to be determined.

The experiments described show different aspects of the PDES sample. Large-scale deformation of $\beta$-PDES results in a considerable decrease of the apparent viscosity, which can be explained by 'crystallite' alignment of the anisotropic material. The viscosity of $\mu$-PDES is considerably higher than that of the isotropic melt, independently of the shear-rate and orientation effects. The $\mu$-PDES was viscoelastic, although the molecular weight of the investigated sample was too low to observe elastic behaviour of the isotropic melt. The observation of a recoverable compliance and the increase in shear viscosity on the formation of $\mu$-PDES is equivalent to some physical crosslinking. Three deformation processes are indicated: orientation of anisotropic domains, viscous deformation of the oriented sample, and recoverable elastic deformation.

DISCUSSION

The observed changes of the molecular structure and segmental motions of the different PDES modifications can be correlated with the changes in mechanical properties and the results from thermal analysis.

The two polymorphs can be distinguished clearly in the crystalline state below the lower disordering transition by n.m.r. spectroscopy. The large differences that we observed in the chemical shifts indicate significant differences in the molecular packing and chain conformations. This appears to be in agreement with different crystal structures as observed by X-ray experiments on $\alpha$- and $\beta$-PDES samples. No mobility of the backbone was observed while the onset of oscillations around the Si-C bond is indicated by partial averaging of the $^{13}$C chemical shift anisotropy.
Mesomorphism, structure and dynamics of PDES. G. Kögler et al.

Figure 5 Optical birefringence of PDES at 300 K in the $\alpha$-phase (a) before and (b) after shearing

![Image of optical birefringence](image)

Figure 6 Creep recovery experiment with $\mu$-PDES at 300 K, shear stress $\sigma = 30000$ dyn cm$^{-2}$; (a) shearing time $t = 14400$ s; (b) shearing time $t = 134000$ s

![Graph of creep recovery experiment](graph)

Figure 7 Temperature dependence of the steady-state viscosity $(\eta = \sigma_0/\gamma)$ of PDES

![Graph of temperature dependence of viscosity](graph)

Significant changes in the molecular conformation of the $-Si-O-$ backbone were observed by the n.m.r. experiments at the $\alpha_1-\alpha_2$ and the $\beta_1-\beta_2$ transition. In contrast, X-ray experiments on oriented $\alpha$- and $\beta$-PDES samples showed practically no change in the identity period and X-ray density on the $\alpha_1-\alpha_2$ and the $\beta_1-\beta_2$ transition, from which the conclusion on similar segment conformations was drawn. The observed onset of restricted backbone librations is in agreement with Raman$^7$ and $^1$H n.m.r.$^{11,12}$ data, which have been reported before.

Considerable averaging of the overlapping $^{13}$C CSA values and the observed coalescence of the isotropic $^{13}$C chemical shifts, which represent the fast exchange average of the Si–C bond rotational isomeric states, demonstrate dynamically the disorder of the side-chain conformation. The motional states appear to be similar or even identical for $\alpha$- and $\beta$-PDES. Although high-resolution $^{29}$Si and $^{13}$C n.m.r. experiments discriminated $\alpha_2$-PDES and $\beta_2$-PDES clearly, the difference in the isotropic chemical shifts is small and vanishes with increasing temperature. This indicates that the difference in segmental molecular structure is small and should vanish already below the transition to the $\mu$-phase.

Conversion of $\alpha_2$-PDES to the thermodynamically more stable $\beta_2$-PDES is unexpectedly slow considering the correlation times of the observed molecular motions.
dependence has been reported for the isotropization equilibrium in polysiloxanes. A strong molecular-weight distribution may be due to the broad molecular-weight distribution and especially to the content of cyclic molecules, which are present due to the chain-ring distribution and especially to the content of cyclic fraction increases with temperature. This partial isotropization may be due to the broad molecular-weight distribution, and also the densities of the μ-state and the isotropic melt do not differ considerably. Owing to the similarity in the free energy and the dynamic nature of both states, we have to consider substantial fluctuation of molecules between the μ-state and the isotropic state, which might help to stabilize the spatial coexistence of the two states. To understand these phenomena better, it appears of great importance to perform similar experiments on samples that are of uniform molecular weight and do not contain cyclic molecules.

Recent experiments, which we shall report in a forthcoming paper, showed the same coexistence of isotropic and anisotropic fractions for poly(di-n-propylsiloxane) and also for poly(di-n-butylsiloxane). Thus, the poly(di-n-alkylsiloxanes) represent a class of materials with novel anisotropic properties. The molecular-weight dependence of the width and the temperature of the isotropization transition in connection with the reported effects on the viscosity offers intriguing possibilities to design materials with particular temperature and shear-rate dependences of their viscoelastic properties.

While this paper was in preparation we got notice of molecular mechanics calculations on PDES, whose results agree nicely with the data and interpretation reported above. In summary, because of the steric hindrance of the ethyl group rotation, cooperative side motion dominates the molecular dynamics in the conformational disordered states and contributes to an apparent chain stiffness.

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REFERENCES

Mesomorphism, structure and dynamics of PDES: G. Kögl er et al.

8 Kögl er, G., Hasenhindl, A. and Möl ler, M. Macromolecules 1989, 22, 4190
15 Cory, D. G. and Ritcey, W. M. Macromolecules 1989, 22, 1611
17 Mark, J. E. J. Chem. Phys. 1968, 49, 1398
20 Sun, D. C. and Magill, J. H. Polymer 1987, 28, 1243
21 Miller, R. D. Chem. Rev. 1989, 1359