Columnar mesophase behaviour of poly(dibutylsiloxane) and related copolymers containing polar substituents

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SUMMARY

The columnar mesophase formation of poly(dibutylsiloxane) (PDBS) was studied with respect to the influence of molecular weight. Additionally, the synthesis of random copolymers containing dibutylsiloxane and butyl(3-cyanopropyl)siloxane units was performed in order to examine the influence of side group polarity on the columnar mesophase behaviour without disturbing the overall molecular geometry. Introduction of 6% 3-cyanopropyl groups appeared to hinder crystallization while copolymers containing 17% 3-cyanopropyl groups did not show crystallization at all. All copolymers formed a columnar mesophase which seemed to gain stability from the presence of the polar substituents.

Introduction

Poly(di-n-alkylsiloxanes) substituted with ethyl to hexyl groups are known to form hexagonal columnar mesophases\textsuperscript{1-4). Similar columnar mesophases have been found for a number of polysilylenes and polyphosphazenes\textsuperscript{5-9). In all cases the molecular structure is constituted of an inorganic flexible backbone substituted by organic side groups. Yet, the question as to how the formation of the columnar mesophase depends on the molecular structure has not been answered satisfactorily. So far, the phase behaviour of polysiloxanes has been studied with respect to the influence of the length of the alkyl side group\textsuperscript{1-4). While poly(diheptylsiloxane) (PDHepS) displayed partial molecular ordering under stress, which was evidenced by a strong birefringence, this feature disappeared for homologues with octyl and higher alkyl substituents\textsuperscript{4).}

Introduction of minor structural irregularity as in random copoly(dipentylsiloxane/dihexylsiloxane)\textsubscript{s} reduced the polymer crystallizability, whereas in copoly(di-butylsiloxane/dihexylsiloxane)\textsubscript{s} the columnar phase behaviour was impeded as well\textsuperscript{10). Another structural aspect concerns the intermolecular interaction forces. In poly(di-n-alkylsiloxanes) these are mainly governed by the apolar alkyl side groups and can be expected to be weak and dispersive.

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In the present work, random copolymers consisting of dibutylsiloxane- and butyl(3-cyanopropyl)siloxane units have been prepared in order to examine the effect of increased intermolecular interaction on the mesophase behaviour. Steric effects may be neglected because of the comparable length of the butyl group and the 3-cyanopropyl group. Based on enthalpic considerations, the increase in intermolecular interactions might be expected to stabilize the columnar mesophase.

In a first step, the columnar mesophase formation of poly(dibutylsiloxane) (PDBS) was evaluated in dependence of the molecular weight and compared to the data of polydiethylsiloxane (PDES) and poly(dipropylsiloxane) (PDPS). In a second step, variations in the thermal behaviour were studied in dependence of the content of the polar 3-cyanopropyl substituents. The polar groups are also of interest because they can be used to modify the polymer, e.g., to make it suitable to practical applications which exploit the partially ordered columnar mesophase.

Experimental part

Materials

Zinc oxide (Merck, 99%), silicagel-60 (Merck), diethyl ether (Merck, p.a.) and ethyl acetate (Merck p.a.) were used as received. Cesium hydroxide monohydrate (Aldrich), was dried in situ on a $5 \times 5$ mm$^2$ stainless steel platelet under high vacuum conditions at elevated temperatures before employing it as an initiator. The synthesis of dibutyl dichlorosilane and butyldichloro(3-cyanopropyl)silane was described elsewhere.

Pentabutyl(3-cyanopropyl)cyclotrisiloxane (1)

A 500 mL three neck flask, equipped with a stirring bar, dropping funnel and reflux condenser was charged with 28.5 g (0.35 mol) ZnO in 270 mL ethyl acetate. Under vigorous stirring, a solution of 9.88 g (0.044 mol) butyldichloro(3-cyanopropyl)silane and 46.85 g (0.22 mol) dibutyldichlorosilane in 50 mL ethyl acetate was added at room temperature over a period of 2.5 h, followed by stirring for another 0.5 h. The mixture was filtered, neutralized with sodium bicarbonate solution and extracted with diethyl ether. After evaporation of the solvent, the crude product was dissolved in hexane and the cyanosubstituted cyclosiloxanes were separated from the unsubstituted products by means of column separation over silica gel with hexane and subsequently ethyl acetate as an eluent.

Distillation afforded 6.51 g (30.5%) of 1 (purity 97% GLC), b.p. 144–150°C (<0.1 mm).

$^1$H NMR (250 MHz): $\delta = 2.37 \ (t; \ J = 7.4 \ Hz, \ 2H, -CH_2CN), 1.82–1.70 \ (m; \ 2H, -CH(CH_2)_3CN), 1.45–1.25 \ (m; \ 20H, Si(CH_2)_3CH_2Si(CH_2)_3CN), 0.90 \ (t; \ J = 6.8 \ Hz, \ 15H, Si(CH_2)_3CH_3), 0.79–0.72 \ (m; \ 2H, Si(CH_2)_3Si(CH_2)_3CN), 0.67–0.53 \ (m; \ 10H, Si(CH_2)_3CH_2CH_3).

$^{13}$C NMR (63 MHz): $\delta = 119.51$ (C4'), 26.15–26.13, 25.07–24.72 (C2, C3), 20.31, 19.54 (C2', C3'), 15.78–15.55 (C1, C1'), 13.73–13.68 (C4).

Distillation of the apolar fraction yielded 12.7 g (60.9%) hexabutylcyclotrisiloxane (purity 99.7% GLC), b.p. 120–128°C (<0.1 mm).
Polymerization

The ring-opening polymerization of the nitrile functionalized cyclotrisiloxane was performed via anionic polymerization in the bulk at 150 °C using cesium hydroxide as the initiator \(^{13}\). The copolymers were prepared by mixing hexabutylicyclotrisiloxane and I in the appropriate molar ratio.

Methods

Gas-liquid chromatography (GLC): Analytical gas chromatography was performed on a Varian 3400 instrument, equipped with a DS 654 data station. A DB-5 capillary column was used (30 m × 0.32 mm × 0.25 μm) in combination with a flame ionization detector (FID). Injection: on column, injector temperature: 70 °C - 100 °C/min - 290 °C; column: 60 °C (3 min) - 10 °C/min - 290 °C; detector: 295 °C. Gas flow: 3 mL/min N₂.

Gel-permeation chromatography (GPC) measurements were carried out in toluene, using Waters microstyragel columns (pore size 10³, 10⁴, 10⁵, 10⁶ Å). Molecular weights were determined by universal calibration, based on narrowly dispersed polystyrene standards \(^{14, 15}\). A dual detection system consisting of a differential refractometer (Waters model 410) and a differential viscometer (Viscotek model H502, UNICAL software) allowed simultaneous determination of molecular weight, molecular-weight distribution and intrinsic viscosity [η].

Calorimetry: A Perkin-Elmer DSC-7 equipped with a PE-7700 computer and TAS-7 software was used to monitor the thermal transitions at scan rates between 5 to 10 K/min. Sample weights were typically chosen between 2 and 5 mg. Transition entropies were calculated assuming equilibrium i.e. \(\Delta H = T \cdot \Delta S\). Cyclohexane, gallium and indium were used as the calibration standards. Transition temperatures are represented by the onset of the recorded endotherm on heating.

Optical polarizing microscopy was performed using a Leitz Ortholux II Pol BK microscope equipped with a Mettler FP 82 hot stage.

NMR spectroscopy: Solution \(^1\)H and proton decoupled \(^{13}\)C NMR spectra were recorded on a Bruker AC 250 spectrometer at 250,1 MHz and 62,8 MHz, respectively. CDCl₃ was used as solvent and tetramethyilsilane (TMS) as a reference. C₁ and C₁′ refer to the carbon atoms attached to the silicon atom and belong to the butyl and 3-cyanopropyl group, respectively. Assignment of \(^{13}\)C resonances are based on 2D correlation experiments reported before on n-alkyl substituted polysilylenes \(^{16}\).

Wide-angle X-ray diffraction studies of the 6/94 copoly[buty1(3-cyanopropyl)siloxane/dibutylsiloxane] were performed using Ni-filtered CuKα radiation. Temperature-dependent diffractograms were recorded on a circular film with a radius of 57,3 mm, using a Guinier-Simon camera as described before \(^4\). Optical density data were collected from the photographically obtained patterns using a linear microdensitometer LS20 (Delft Instruments) controlled by SCANPI software.

Results and discussion

Monomer synthesis

The synthesis of pentabutyl(3-cyanopropyl)cyclotrisiloxane (I) was performed by the ZnO mediated condensation of butyldichloro(3-cyanopropyl)silane in the presence of 5 equivalents of dibutylchlorosilane \(^{12, 13}\). This reaction was exothermic and was carried out at room temperature. As the main side product, hexabutylicyclotrisiloxane was formed together with higher butyl substituted cyclosiloxanes. The nitrile
substituted derivative was readily separated from hexabutyldicyclotrisiloxane by means of column fractionation, and it was purified by distillation.

**Polymerization**

The ring-opening polymerization of cyclosiloxane is known to be hindered by redistribution reactions, which lead to the formation of cyclic by-products\(^\text{17,18}\). The synthesis of the polymers is kinetically controlled and in order to obtain high polymer yields, the ring-opening polymerization reaction should be carried out in bulk using reactive monomers which display high rates of polymerization. Furthermore, the reaction should be stopped before the mixture has reached its equilibrium composition. Equilibrium polymerizations of (MeRSiO)\(_n\), in which R is varied along the series H, CH\(_3\), CH\(_2\)CH\(_3\), phenyl and CH\(_2\)CH\(_2\)CF\(_3\), have been shown to yield cyclic material with weight fractions of 12,5, 18,3, 25,8, 30,0 and 82,7%, respectively\(^\text{17,18}\). These values indicate an increasing tendency towards ring formation with larger substituent sizes. The anomalously high equilibrium ring concentration in case of trifluoropropyl substitution demonstrates an additional influence exerted by the electronegative trifluoromethyl moiety.

Poly(dibutylsiloxane) was prepared by anionic ring-opening polymerization of hexabutyldicyclotrisiloxane with CsOH as an initiator. Yields of the crude polymer were in the order of 70% with a polydispersity of 2. A series of poly(dibutylsiloxane) samples with different molecular weights was prepared by fractionation of the polymer from toluene using methanol as the non-solvent. Molecular weight, polydispersity and intrinsic viscosity of various fractions are summarized in Tab. 1.

Pentabutyl(3-cyanopropyl)cyclotrisiloxane (1) was polymerized via a similar process. Three copolymers were prepared containing 6%, 8% and 17% 3-cyanopropyl groups, respectively, by mixing the nitrile substituted cyclotrisiloxane with hexabutyldicyclotrisiloxane in the appropriate molar ratio. The crude polymers were repeatedly fractionated from toluene/ethanol to obtain narrowly distributed samples. Copolymer compositions were determined by means of \(^1\)H NMR spectroscopy and are summarized in Tab. 2 together with molecular weight, polydispersity and intrinsic viscosity. Fig. 1 depicts the \(^1\)H and \(^{13}\)C NMR spectra of the 17/83 copoly[buty](3-cyanopropyl)siloxane/dibutylsiloxane.
Tab. 1. Mass-average molar mass ($\bar{M}_w$), ratio of mass- to number-average molar masses ($\bar{M}_w/\bar{M}_n$), intrinsic viscosity and transition temperatures of fractionated poly(dibutylsiloxane) samples

<table>
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<tr>
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<th>$\bar{M}_w/\bar{M}_n$</th>
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a) From gel-permeation chromatography according to universal calibration.
b) Onset temperature in differential scanning calorimetry heat scan.
c) Disappearance of birefringence.

Tab. 2. Chemical composition, mass-average molar mass, $\bar{M}_w/\bar{M}_n$ and intrinsic viscosity of random copoly[butil(3-cyanopropyl)siloxane/dibutylsiloxane]

<table>
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<th>$\bar{M}_w/\bar{M}_n$</th>
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<td>dL/g</td>
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<td>17</td>
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</tr>
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<td></td>
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</table>

a) According to $^1$H NMR spectroscopy.
b) From gel-permeation chromatography according to universal calibration.

Melting behaviour

The melting behaviour of poly(dibutylsiloxane) was investigated with respect to the influence of molecular weight. All samples were cooled from 353 K to 195 K at a rate of 10 K/min, annealed for 5 min and then heated at a rate of 10 K/min to 353 K. Fig. 2 depicts the DSC cooling and heating scans of poly(dibutylsiloxane) with $\bar{M}_w =$
128000 g/mol. In the DSC heating scan two endotherms can be discerned with onset temperatures of 238 K and 262 K, corresponding to a crystal-crystal and to a crystal-mesophase transition, respectively.

According to solid state $^{29}$Si and $^{13}$C NMR spectroscopy measurements, the first transition characterizes the onset of side group mobility, whereas the second transition indicates formation of the hexagonal columnar mesophase\textsuperscript{2).} Above the second transition strong birefringence was observed until a temperature of 572 K, at which temperature the polymer underwent isotropization.

The three transitions appeared to be molecular weight dependent, which is shown in Fig. 3. While the molecular weight dependence of the disordering transitions remained limited, the isotropization temperature increased considerably with increasing molecular weight. This is in line with the observations reported on poly(diethylsiloxane) and poly(dipropylsiloxane)\textsuperscript{1).} When the isotropization temperature is plotted
Columnar mesophase behaviour of poly(dibutylsiloxane) . . .

Fig. 2. DSC cooling and heating scans of poly(dibutylsiloxane) (rate 10 K/min)

Fig. 3. Molecular weight dependence of the transition temperatures of poly(dibutylsiloxane)

as a function of the reciprocal molecular weight, a linear relation is observed which upon extrapolation to zero yields the isotropization temperature of 592 K for poly(dibutylsiloxane) of infinite molecular weight (Fig. 4)\(^\text{19}\).

Quenching of a poly(dibutylsiloxane) sample from the columnar mesophase at 323 K by putting it into liquid N\(_2\), yielded the DSC heating scan depicted in Fig. 5. Two recrystallizations can be observed with onset temperatures at 179 K and 212 K, followed by the disordering transitions described above. This peculiar cold-crystallization effect has also been observed for poly(dipentylsiloxane) (PDPeS) upon quenching from the columnar mesophase but not for other members of the group of
columnar mesomorphic poly(di-alkylsiloxane)s. The present measurements suggest that the effect is due to vitrification of the mesophase, which undergoes a two-step recrystallization process (vide infra).

The melting behaviour of the copolymers containing various amounts of nitrile groups was investigated by cooling the samples from 293 K to 163 K at a rate of 10 K/min, followed by heating at the same rate (Fig. 6). The heating scans of the copolymers containing 6 and 8% nitrile groups displayed recrystallization exotherms similar to those observed for the poly(dibutylsiloxane) homopolymer after quenching from the columnar mesophase state (Fig. 5). These were followed by only one single
endotherm at 224 K and 217 K for the two copolymers, respectively. No other transitions were visible until the isotropization temperature at 590–610 K was reached. The 17/83 copoly[buty1(3-cyanopropyl)siloxane/dibutylsiloxane] did not show any crystallization, respectively disordering transitions, in the DSC scans. This resembles the behaviour of 70/30 copoly(dipentylsiloxane/dihexylsiloxane)10, where the absence of crystallization is caused by the difference in chain length of the alkyl side groups. Since butyl groups and 3-cyanopropyl groups have nearly the same length, it must be assumed that dipolar interactions play an important role in preventing the polymer from crystallizing.

Comparison of the transition enthalpies of PDBS and of the copolymers containing 6% or 8% 3-cyanopropyl groups indicated that formation of the high temperature crystalline phase is suppressed by the presence of polar moieties. The limited stability of this phase has already been observed in PDBS samples which contained low amounts of cyclic oligomers and which did not show a second disordering transition in the DSC heating scan. This transition could only be observed after purification of the samples.

The observation of the two cold crystallization transitions for copolymers containing 6% and 8% butyl-3-cyanopropyldiisoxane units resembles the behaviour of PDBS and PDPeS homopolymers after they had been quenched from the columnar mesophase2. Although the effect was not quite understood, it was assumed that it is due to simultaneous vitrification of two fractions of material differing in their molecular mobility, e.g. columnar and amorphous3 or columnar and partially crystalline4. In view of the high isotropization temperature of the fractionated copolymers, it is unlikely that they contain amorphous material. In addition, formation of the high temperature crystalline phase is not observed. It follows that the cold-crystallization effects are caused by some two-step crystallization process of the vitrified columnar mesophase itself.

In order to investigate the hindered crystallization of the copolymers containing nitrile moieties, the crystal structure of the 6/94-copoly[buty1(3-cyanopropyl)siloxane/dibutylsiloxane] was studied by temperature dependent wide-angle X-ray diffraction (WAXD) experiments (Fig. 7)20. After 30 min annealing at −100 °C, a large number of reflections is observed which hints at a well developed crystalline structure, differing considerably from that of PDBS20. Upon heating, a continuous transformation into the columnar mesophase state is observed, without formation of
an intermediate high temperature crystal phase, which is consistent with the DSC results. For the columnar mesophase a nearly hexagonal unit cell is proposed with the $a$-parameter of 12.15 Å, i.e., similar to what has been observed for the PDBS homopolymer. The recrystallization transitions which were visible in the DSC heating traces have not been observed by WAXD due to the long annealing times which have been used in order to approach equilibrium conditions.

Despite interference of the nitrile substituents with the crystallization process, a strong birefringence could be observed for all copolymers, which lasted until 608 K, i.e., even beyond the isotropization temperature of pure poly(dibutylsiloxane).

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Fig. 7. Temperature dependent wide-angle X-ray diffractograms of 6/94-copoly[butyl(3-cyanopropyl)siloxane/dibutylsiloxane]

Fig. 8. Optical polarizing micrograph of 17/83 copoly[butyl(3-cyanopropyl)siloxane/dibutylsiloxane] after isotropization and 1 min annealing at 571 K
Isotropization, followed by cooling to 571 K and annealing for 1 min, resulted in formation of the same texture as observed for pure poly(di-n-alkylsiloxane)s, i.e., lamellae with thicknesses in the order of 5–15 μm consisting of extended-chain molecules (Fig. 8)\textsuperscript{1,4,19}.

Conclusions

Random copoly(dibutylsiloxane)s containing various amounts of butyl-3-cyanopropylsiloxane units were prepared by anionic ring-opening polymerization of mixed cyclotrisiloxanes with cesium hydroxide. The introduction of 3-cyanopropyl groups hindered the crystallization but did not interfere with the formation of the columnar mesophase. In view of the comparable length of butyl and 3-cyanopropyl groups, the reduced crystallizability is presumably caused by the presence of dipolar interactions rather than by geometrical molecular irregularity. The isotropization temperature displayed by the nitrile containing copolymers was slightly higher than for the parent poly(dibutylsiloxane), even for copolymer samples with relatively low molecular weights. Hence, it might be concluded that the intermolecular dipolar interactions stabilize the columnar mesophase.

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\end{itemize}