Random Copoly(di-*n*-alkylsiloxane/di-*n*-hexylsiloxane)s: Synthesis and Columnar Mesophase Formation

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ABSTRACT: High molecular weight samples of random copoly(di-*n*-alkylsiloxane/di-*n*-hexylsiloxane)s containing either diethylsiloxane, di-*n*-butylsiloxane, or di-*n*-pentylsiloxane comonomeric units have been prepared and investigated with respect to their ability to form a hexagonal columnar mesophase. A random substitution of the polysiloxane main chain has been achieved by cationic ring-opening polymerization of mixed cyclic trimers consisting of di-*n*-alkylsiloxane and di-*n*-hexylsiloxane units. Structural irregularities caused by introduction of di-*n*-alklysiloxane units destabilized the crystalline phase, as demonstrated by a lowering of the transition temperatures and by a decrease of the transition enthalpies. All copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s retained the ability of the homopolymers to form a columnar mesophase. However, when the difference in alkyl side group length exceeded one carbon atom, the columnar mesophase behavior was not displayed.

Introduction

In previous articles, we described the mesomorphic behavior of symmetrically substituted poly(di-*n*-alkylsiloxane)s.[1−4] Unlike poly(dimethylsiloxane) (PDMS), polysiloxanes symmetrically substituted with longer alkyl side groups exhibited intermediate formation of a columnar mesophase.[1−6] For poly(diethylsiloxane) (PDES), it has been found that the transition from the columnar phase into the isotropic melt contributed only 3% to the total melting entropy,[1,5] which illustrates the high amount of disorder present in the mesophase. Introduction of irregularities within the molecular architecture would influence the packing efficiency of the polymer molecules and thus might introduce even more disorder within the mesophase. In order to study the impact of this constitutional disorder on the columnar mesophase behavior, random copoly(di-*n*-alkylsiloxane/di-*n*-hexylsiloxane)s containing either diethylsiloxane, di-*n*-butylsiloxane, or di-*n*-pentylsiloxane units have been synthesized and investigated with regard to their thermal behavior.

Experimental Section

Materials. Di-*n*-alkyldichlorosilanes have been prepared by hydrosilylation of 1-alkenes with dichlorosilane in the presence of hexachloroplantinic acid.[7] Zinc oxide (Merck, 99%) and ethyl acetate (Merck, 99%) were used as received. Trifluoromethanesulfonic acid (Alfa) was freshly distilled under vacuum before its use as an initiator.

Monomers. Cyclic comonomers which were used in the preparation of random copolysiloxanes have been prepared by cocondensation of two different di-*n*-alkyldichlorosilanes with zinc oxide in ethyl acetate.[8] As an example, the preparation of 1,1′-diethyl-3,3′,5,5′-tetra-*n*-hexylcyclotrisiloxane is described.

1,1′-Diethyl-3,3′-5,5′-tetra-*n*-hexylcyclotrisiloxane. A 500 mL three-neck flask equipped with a reflux condenser, dropping funnel, and stirring bar was charged with 36.7 g (0.45 mole) of zinc oxide in 120 mL of ethyl acetate. Over a period of 1 h, a solution of 54 g (0.2 mol) of di-*n*-hexyldichlorosilane and 16 g (0.1 mol) of diethyldichlorosilane in 80 mL of ethyl acetate was added, during which time the temperature of the mixture increased to approximately 50 °C. After the addition was complete, stirring was continued for 1 h. The mixture was then neutralized by pouring it slowly into 250 mL of a saturated sodium bicarbonate solution under vigorous stirring. The suspension was filtered and the filtrate was extracted with diethyl ether. The combined organic phases were dried over $\mathrm{Na_2SO_4}$, and the solvent was evaporated. The crude condensation product was purified by distillation. Isolated yield, 10 g (19%) of 1,1′-diethyl-3,3′,5,5′-tetra-*n*-hexylcyclotrisiloxane (purity 92%, GLC); bp 162−168 °C/0.1 mmHg; NMR (δ, relative to TMS): ^{1}H NMR (250 MHz), 1.48−1.20 (m, 32H, $\mathrm{(CH_2)_4}$), 0.98 (t, $J = 7.9$ Hz, 6H, $\mathrm{SiCH_2C}H_3$), 0.88 (t, $J = 7.1$ Hz, 12H, $\mathrm{Si(CH_2)_5C}H_3$), 0.58 (t, $J = 7.5$ Hz, 12H, $\mathrm{SiC}H_2\mathrm{CH_3}$ and $\mathrm{SiC}H_2\mathrm{(CH_2)_4CH_3}$); ^{13}C NMR (62.9 MHz), 32.96 (C3), 31.61 (C4), 22.62, 22.59 (C5, C2), 16.21 (C1), 14.12 (C6), 7.45 (C1′), 6.25 (C2′); ^{29}Si NMR (79.5 MHz), −9.50 ($\mathrm{OSi(C_2H_5)_2}$), −10.46 ($\mathrm{OSi(C_6H_{13})_2}$), relative intensity 1:2.

1,1′-*Di-n*-hexyl-3,3′,5,5′-tetraethylcyclotrisiloxane. Isolated yield, 17% (purity 95.6%, GLC); bp 110−115 °C/0.1 mmHg; NMR (δ, relative to TMS): ^{1}H NMR (250 MHz), 1.48−1.20 (m, 16H, $\mathrm{(CH_2)_4}$), 0.99 (t, $J = 7.9$ Hz, 12H, $\mathrm{SiCH_2C}H_3$), 0.88 (t, $J = 7.1$ Hz, 6H, $\mathrm{(CH_2)_5C}H_3$), 0.58 (t, $J = 7.5$ Hz, 12H, $\mathrm{SiC}H_2\mathrm{CH_3}$ and $\mathrm{SiC}H_2\mathrm{(CH_2)_4CH_3}$); ^{13}C NMR (62.9 MHz), 32.95 (C3), 31.59 (C4), 22.61 (C5, C2), 16.19 (C1), 14.12 (C6), 7.46 (C1′), 6.24 (C2′); ^{29}Si NMR (79.5 MHz), −9.33 ($\mathrm{OSi(C_2H_5)_2}$), −10.33 ($\mathrm{OSi(C_6H_{13})_2}$), relative intensity 2:1.

Four cyclic comonomers consisting of di-*n*-butylsiloxane and di-*n*-hexylsiloxane units with respectively di-*n*-pentylsiloxane and di-*n*-hexylsiloxane units were prepared by condensation of equimolar amounts of the respective di-*n*-alkyldichlorosilanes with 1.5 equiv of zinc oxide in ethyl acetate. Due to the small difference in boiling point between the four different cyclotrisiloxanes which were formed, these comonomers could not be obtained as pure compounds. Instead, distillation of the crude condensation product afforded different fractions containing various cyclotrisiloxanes.

Polymers. High molecular weight copolymers were prepared by cationic ring-opening polymerization of a defined mixture of cyclic trimers using trifluoromethanesulfonic acid as the initiator. In a typical polymerization setup, a 50 mL two-neck flask, equipped with an argon inlet, septum, and a

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stirring bar, was charged with 2 g of a defined mixture of two comonomers. The mixture was degassed and flushed with argon, and subsequently 1 μL of trifluoromethanesulfonic acid was added via the septum. After 4 h of stirring at room temperature, formation of high molecular weight material became evident by the increase in viscosity. Normally, the mixture was allowed to react for 36 h before workup. Crude polymerization products were dissolved in toluene and reprecipitated twice in refluxing ethanol to remove traces of initiator and oligomeric side products. Crude polymer yields were on the order of 65–75%. After fractionation in toluene/ethanol, the fractions were dried under vacuum at 110 °C for at least 24 h.

Methods. 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 m) 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 N_2.

GPC measurements were carried out in toluene using μ-Styragel columns with pore sizes of 10^5, 10^4, 10^3, and 10^6 Å (Waters). Elution volumes were correlated to molecular weights by universal calibration based on polystyrene standards.[9,10] 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 weights, molecular weight distributions, and intrinsic viscosities $[\eta]$.

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 and 10 K/min. Sample weights were typically chosen between 5 and 10 mg. Transition entropies were calculated assuming equilibrium, i.e., $\Delta H = T\Delta S$. Cyclohexane, gallium, and indium were used as calibration standards. Listed transition temperatures represent the onset of the recorded endotherms upon heating.

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

NMR. Solution ^{1}H and proton-decoupled ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer at 250.1 and 62.8 MHz, respectively. ^{29}Si NMR spectra were recorded on a Varian 400 WB spectrometer at 79.5 MHz. Relaxation times of 80 s were chosen to ensure near to complete relaxation of the ^{29}Si nuclei between successive scans. In all cases, $CDCl_3$ was used as a solvent and TMS as a reference. The denotation C1 refers to the carbon atom attached to the polymer main chain. High-resolution solid-state ^{29}Si NMR measurements were carried out as described before on a Bruker CXP 300 spectrometer at 59.63 MHz.[1,2] Temperatures were measured by a thermocouple adjacent to the rotor with an accuracy of ±10 K.

X-ray Diffraction. Wide-angle diffraction patterns of the copolymers were obtained at room temperature, using nickel-filtered Cu Kα radiation. Slightly pressed flat samples were mounted perpendicularly to the primary X-ray beam. A flat-film camera with a sample–film distance of 90 mm was used to record the reflections. Optical density data were collected from the photographically obtained patterns using a linear scanning microdensitometer LS20.

Results and Discussion

Synthesis. The formation of polymeric products during the ring-opening polymerization of hexa-*n*-alkylcyclotrisiloxanes is kinetically controlled.[11] In order to obtain high polymer yields, the reaction has to be stopped before equilibrium occurs. Especially in the case of long *n*-alkyl substitutents, the equilibrium state is strongly in favor of cyclic oligomers. Hence, random copoly(di-*n*-alkylsiloxane)s of high molecular weight cannot be obtained by scrambling of the different di-*n*-alkylsiloxane units in the equilibrium state.[12] Instead, polymerization was performed using defined mixtures of cyclic comonomers in which the different substituted siloxane units were already combined. These comonomers were prepared by cocondensation of the respective di-*n*-alkyldichlorosilanes.

Table 1. Cyclic Comonomers $[(R^1_2SiO)(R^2_2SiO)_2]$

R^1	R^2	bp (°C/mmHg)	yield (%)	D_3 content (%)
n-hexyl	ethyl	110–115/0.1	17	96
ethyl	*n*-hexyl	162–168/0.1	19	92
n-hexyl	*n*-butyl	148–178/0.1	23	97 Bu_2SiO: 60% Hex_2SiO: 40%
n-butyl	*n*-hexyl	178–190/0.1	17	98 Bu_2SiO: 33% Hex_2SiO: 67%
n-hexyl	*n*-pentyl	185–195/0.1	9	89 Pe_2SiO: 75% Hex_2SiO: 25%
n-pentyl	*n*-hexyl	195–210/0.1	13	85 Pe_2SiO: 47% Hex_2SiO: 53%

$$R^1{}_2SiCl_2 + R^2{}_2SiCl_2 + ZnO \xrightarrow{EtOAc/RT} [(R^1{}_2SiO)_{3-n}(R^2{}_2SiO)_n] + ZnCl_2 \qquad n = 0-3$$

The formation of the strained cyclotrisiloxane appeared to be favored kinetically at the heterogeneous contact with the finely divided ZnO particles, a process which might also be facilitated by the steric repulsion between the side groups. Apart from the cyclic trimer, higher cyclic oligomers like the tetramer and pentamer were formed in a weight ratio of approximately 60:20:5. The remainder consisted of intractable oligomeric material. During comonomer synthesis, the crude condensation product consisted of a mixture of four different cyclotrisiloxanes, which were separated by distillation into fractions containing various amounts of cyclotrisiloxanes. Results of comonomer synthesis are listed in Table 1.

Polymer synthesis was performed in bulk monomer, using trifluoromethanesulfonic acid as the initiator. The molecular weight distribution of the unfractionated polymer was on the order of 1.8–2.1 according to GPC (yield 65–75%). Within the course of 3–5 days of stirring at room temperature, no significant decrease in viscosity was observed. GLC analysis of the cyclic byproducts indicated that mainly the cyclic hexamer had been formed (10–15%), which points to some endbiting during polymerization.[13,14] Hence it migh be assumed that no significant redistribution occurred during the polymerization process.

$$n(R_2SiO)_3 \xrightarrow{CF_3SO_3H/bulk/RT} [-R_2SiO-]_n$$

Due to the use of monomers in which two different di-*n*-alkylsiloxane units are combined and the presumably very similar reactivity of the comonomers and their respective subunits, especially in the case of *n*-pentyl and *n*-hexyl substitutents, incorporation rates of the two building units can be considered to be equal. As a result, a random composition of the copolymers can be expected. While the similarity of the comonomeric units favors a random structure, it did not allow for investigation of the polymer microstructure in detail. Properties of fractionated copoly(diethylsiloxane/di-*n*-hexylsiloxane)s, copoly(di-*n*-butylsiloxane/di-*n*-hexylsiloxane)s, and copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s are sum-

Table 2. Properties of Fractionated Copoly(diethylsiloxane/di-*n*-hexylsiloxane)s

C^2/C^6 (calc)	C^2/C^6 (^{13}C NMR)	yield (%)	M_w[a]	M_w/M_n[a]	$[\eta]$[b] (dL/g)
10/90	9/91	13	155 200	1.8	0.439
30/70	27/73	6	130 500	1.2	0.425
50/50	49/51	23	102 500	1.2	0.358
70/30	72/28	13	87 790	1.9	0.342
90/10	91/9	6	107 000	1.3	0.443

[a] From GPC according to universal calibration. [b] From online detection upon GPC elution according to universal calibration.

Table 3. Properties of Fractionated Copoly(di-*n*-butylsiloxane/di-*n*-hexylsiloxane)s

C^4/C^6 (calc)	C^4/C^6 (^{13}C NMR)	yield (%)	M_w[a]	M_w/M_n[a]	$[\eta]$[b] (dL/g)
1/99		30	255 000	1.41	0.520
5/95	4/96	29	224 000	1.30	0.494
10/90	8/92	27	244 000	1.30	0.508
25/75	24/76	10	197 000	1.23	0.427
33/67	34/66	27	116 000	1.20	0.289
60/40	61/39	21	127 000	1.25	0.328

[a] From GPC according to universal calibration. [b] From online detection upon GPC elution according to universal calibration.

Table 4. Properties of Fractionated Copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s

C^5/C^6 (calc)	C^5/C^6 (^{13}C NMR)	yield (%)	M_w[a]	M_w/M_n[a]	$[\eta]$[b] (dL/g)
10/90	14/86	51	681 000	1.9	1.175
30/70	31/69	30	431 000	1.8	0.843
50/50	45/55	27	338 000	1.5	0.741
70/30	65/35	37	357 000	1.7	0.711
90/10	83/17	44	394 000	1.6	0.806

[a] From GPC according to universal calibration. [b] From online detection upon GPC elution according to universal calibration.

marized in Tables 2–4, respectively. Average copolymer compositions were determined by solution ^{13}C NMR by comparing the intensities of the terminal methyl carbon signals of the *n*-alkyl side groups. This ratio corresponded reasonably well with calculated values, demonstrating that both comonomers which were present in the reaction mixture participated in the polymerization process.

Thermal Behavior. Within the series of copoly(diethylsiloxane/di-*n*-hexylsiloxane)s, only the copolymer with 10% diethylsiloxane units and 90% di-*n*-hexylsiloxane units was able to crystallize. The DSC heating scan obtained after cooling the sample from 333 to 193 K at 10 K/min, followed by heating at the same rate, showed two transitions located at 248 and 257 K, respectively. Optical polarizing microscopy did not reveal any birefringence at room temperature, which indicated that the latter transition resulted in formation of the isotropic melt. All other copoly(diethylsiloxane/di-*n*-hexylsiloxane)s appeared to be isotropic at room temperature as well. Apparently, the crystallization was impeded above a diethylsiloxane content of 10%, while the difference in side group length of four carbon atoms prevented formation of the columnar mesophase in any case.

Polarizing optical microscopy revealed that of the series of copoly(di-*n*-butylsiloxane/di-*n*-hexylsiloxane)s, only the copolymer containing 1% *n*-butylsiloxane units was able to show birefringence up to a temperature of 598 K. Isotropization followed by annealing at 571 K resulted in formation of band-shaped structures which have been reported to be characteristic for the hexagonal columnar mesophase of flexible chain molecules.[4,6] It should be noted however that in this case the presence of di-*n*-butylsiloxane units could not be ascertained by ^{13}C NMR. When the di-*n*-butylsiloxane content exceeded 5%, materials were obtained which were isotropic at room temperature. Only upon pressing the samples between two glass slides could faint birefringence be observed, which immediately disappeared upon relieving of the stress.

Calorimetric investigations indicated that upon cooling the samples from 393 to 193 K at 10 K/min, crystallization occurred for copolymers with a di-*n*-butylsiloxane content up to 25%. Table 5 summarizes the calorimetric data on the copoly(di-*n*-butylsiloxane/di-*n*-hexylsiloxane)s, as obtained from DSC heating thermograms at heating rates of 10 K/min. Multiple melting transitions, displayed by copolymers with 1 and 5% di-*n*-butylsiloxane units, were also observed for low molecular weight poly(di-*n*-hexylsiloxane) homopolymers.

The thermal behavior of the copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s resembled that of the corresponding poly(di-*n*-pentylsiloxane) and poly(di-*n*-hexylsiloxane) homopolymers.[4] Panels a and b of Figure 1 show the DSC heating and cooling thermograms respectively of the copolymers and of the homopolymers. Homopolymers as well as most of the copolymers showed two disordering transitions, above which the samples remained anisotropic, as demonstrated by the birefringence discussed below. In between the two transitions, the equilibrium state can be considered to be a conformationally disordered 3D crystal (high-temperature crystal phase).[4] Increasing the content of the minor comonomer units leads to copolymers with lower transition temperatures and transition enthalpies. Symmetrical substitution of the polysiloxane chain with 70% *n*-pentyl groups and 30% *n*-hexyl groups yielded a copolymer which could not crystallize anymore at a cooling rate of 10 K/min. Only upon lowering the cooling and heating rate to 5 K/min, recrystallization and melting transitions could be observed.

Upon quenching the copolymer samples from 323 K by putting them into liquid nitrogen, followed by heating from 153 to 323 K at 10 K/min, recrystallization transitions are observed (Figure 1c). Whereas poly(di-*n*-pentylsiloxane) homopolymer exhibited two recrystallization transitions at 185 and 201 K, which have been assigned to recrystallization of a vitrified fraction of the columnar mesophase and of the high-temperature crystal phase, respectively,[4] the copolymers show one recrystallization transition located between 177 and 192 K. The occurrence of only one transition might be explained by recrystallization of a vitrified fraction of hexagonal columnar material. Further recrystallization may be hindered by the irregular molecular constitution of the copolymers. Table 6 summarizes the calorimetric data of the copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s as obtained at cooling and heating rates of 5 K/min.

Optical polarizing microscopy revealed that all copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s were able to form a mesophase. Heating a sample above the isotropization temperature, followed by 1–12 min of annealing at a temperature 50 K below, led to the formation of band-shaped structures (Figure 2), which have also been observed for the polysiloxane homopolymers.[4] The time needed to form these structures was significantly longer for copolymers with intermediate substitution (10–12 min) than for copolymers with low amounts of

Table 5. Thermal Transitions of Copoly(di-*n*-butylsiloxane/di-*n*-hexylsiloxane)s As Observed in DSC Heating Thermograms (Rate 10 K/min)

% butyl	DP[a]	T_{d1} (K)	ΔH_{d1} (kJ/mol)	ΔS_{d1} (J/(K mol))	T_{d2} (K)	ΔH_{d2} (kJ/mol)	ΔS_{d2} (J/(K mol))	T_i[b] (K)
0	6030	246	6.7	27.2	296	5.1	17.2	603
1	1194	199/243	3.2/2.3	16.1/9.4	273/291	8.3/2.5	30.3/8.5	598
4	1063	196/238	5.6/0.6	28.4/2.7	267/282	8.1/0.8	30.4/3.0	
8	1166				259	1.4	5.5	
24	981				219	0.6	2.9	
34	594							
61	703							
100	2013	229	3.6	15.7	254	0.9	3.5	583

[a] Based on M_w. [b] Disappearance of birefringence after annealing the sample for 10–12 min at 30–50 K below T_i.

defects (1 min). Based on previous studies, it is assumed that the bands are to be considered as the lateral faces of lamellar domains with an average thickness on the order of several microns, which consist of extended-chain molecules.[6,15,16] Heating the samples a second time, after a total annealing time of about 15 min, yielded isotropization temperatures which were approximately 15–20 K higher than the previous values, presumably due to formation of larger and better ordered lamellar domains.

As shown in Table 6, the isotropization temperatures appeared to decrease for copolymers with intermediate composition. To check for the influence of molecular weight,[6] isotropization temperatures were also measured for lower molecular weight fractions. These values were found to be similar to the values indicated in Table 6, demonstrating that the decrease in isotropization transition is primarily due to the substitution pattern of the polymer backbone.

The decrease in isotropization transition temperatures is accompanied by a decrease of the crystallization temperatures; thus overall it appears that the temperature regime of the columnar mesophase is not affected by the introduction of irregularities within the molecular architecture (Figure 3).

Wide-Angle X-ray Diffraction. Similar to what has been described for poly(di-*n*-alkylsiloxane) homopolymers,[4-6] X-ray diffraction powder patterns of the copoly(di-*n*-pentylsiloxane/si-*n*-hexylsiloxane)s revealed three reflections for the hexagonal columnar mesophase (Figure 4):

(i) An intense and narrow reflection corresponding to the interplanar spacing d_0 is observed near 7° (2θ), the precise position depending on the composition of the copolymer.

(ii) A narrow and weak reflection, which is not visible in the densitometric trace because of the extremely low intensity, was observed in the patterns from the point collimation camera. The Bragg distance of this reflection could be related to the Bragg distance of the strong reflection (i) according to $d_0/\sqrt{3}$.

(iii) A weak and broad reflection is present between 15 and 25° (2θ), its maximum position corresponding to a Bragg spacing of 4.55 Å.

Besides (i) and (ii), there are no more narrow reflections visible in the patterns. The packing of the copolymer molecules within the columnar mesophase may therefore be characterized as hexagonal and the reflections (i) and (ii) can accordingly be denoted as d_{100} and d_{110}. The distance between the polymer main chains corresponds to the a parameter of the hexagonal unit cell and can be calculated according to $a = 2d_0/\sqrt{3}$. A gradual increase of this distance with increasing di-*n*-hexyl substitution of the polymer main chain is shown in Figure 5. The curve shows an S-shape rather than a stepwise jump, demonstrating that indentation of the side groups occurs in the case of the copolymers with intermediate composition, whereas copolymers containing <17% di-*n*-pentylsiloxane or di-*n*-hexylsiloxane units are packed more or less similarly to the PDHS and PDPeS homopolymers.

Within experimental error, the Bragg distance of reflection (iii) is the same for all copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s. The value coincided with that observed for liquid paraffins or the amorphous phase in semicrystalline polyethylene.[17] In the case of poly(di-*n*-alkylsiloxane)s, it can be correlated to the average lateral approach distance of the alkyl side groups. It is worth mentioning that by pressing the samples during the sample preparation, some orientation could be introduced in the copolymers. From the resulting diffractograms it appeared that reflections (i) and (ii) concentrated along one direction whereas reflection (iii) showed greater intensity along the normal direction. This confirmed that reflection (iii) is due to some poor periodicity along the backbone of the copolymers, whereas reflections (i) and (ii) correspond to the interchain periodicity.

Solid-State ^{29}Si NMR. To investigate changes in conformation and molecular mobility upon phase transitions, the 30/70 copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane) sample was studied by high-resolution solid-state ^{29}Si NMR spectroscopy. Figure 6 shows the temperature-dependent ^{29}Si NMR MAS spectra of this copolymer. Similar to what has been described recently for the behavior of the PDPeS and PDHS homopolymers,[4] this copolymer shows distinct values of the isotropic ^{29}Si chemical shift, which can be assigned to the different phases. Slight broadening of the signals in comparison with the spectra for the homopolymers is caused by the presence of two types of silicon atoms within the copolymer, which are disubstituted either with *n*-pentyl or with *n*-hexyl groups.

Below the first crystal–crystal transition at a temperature of 185 K, two signals are visible at −18.8 and −23.3 ppm, respectively, the second one clearly broader than the first. Both PDPeS and PDHS homopolymers showed only one signal at −19 and −18.7 ppm, respectively, within that same temperature regime. Upon heating, the maximum position of the broad signal shifted upfield to −21.2 ppm, although a shoulder remained at −23.5 ppm. Upon entering the high-temperature crystalline phase, the signal at −18.8 ppm disappeared and two signals remained at −21 and −23.6 ppm, respectively, characteristic for the high-temperature crystalline phase and the columnar mesophase. The presence of a broad signal within the low-temperature crystalline phase at 185 K, with a maximum near −23.3 ppm can be explained by vitrification of the columnar mesophase. This is consistent with the DSC results, which showed the occurrence of a glassy state as a result of the irregular substitution of the polymer main chain

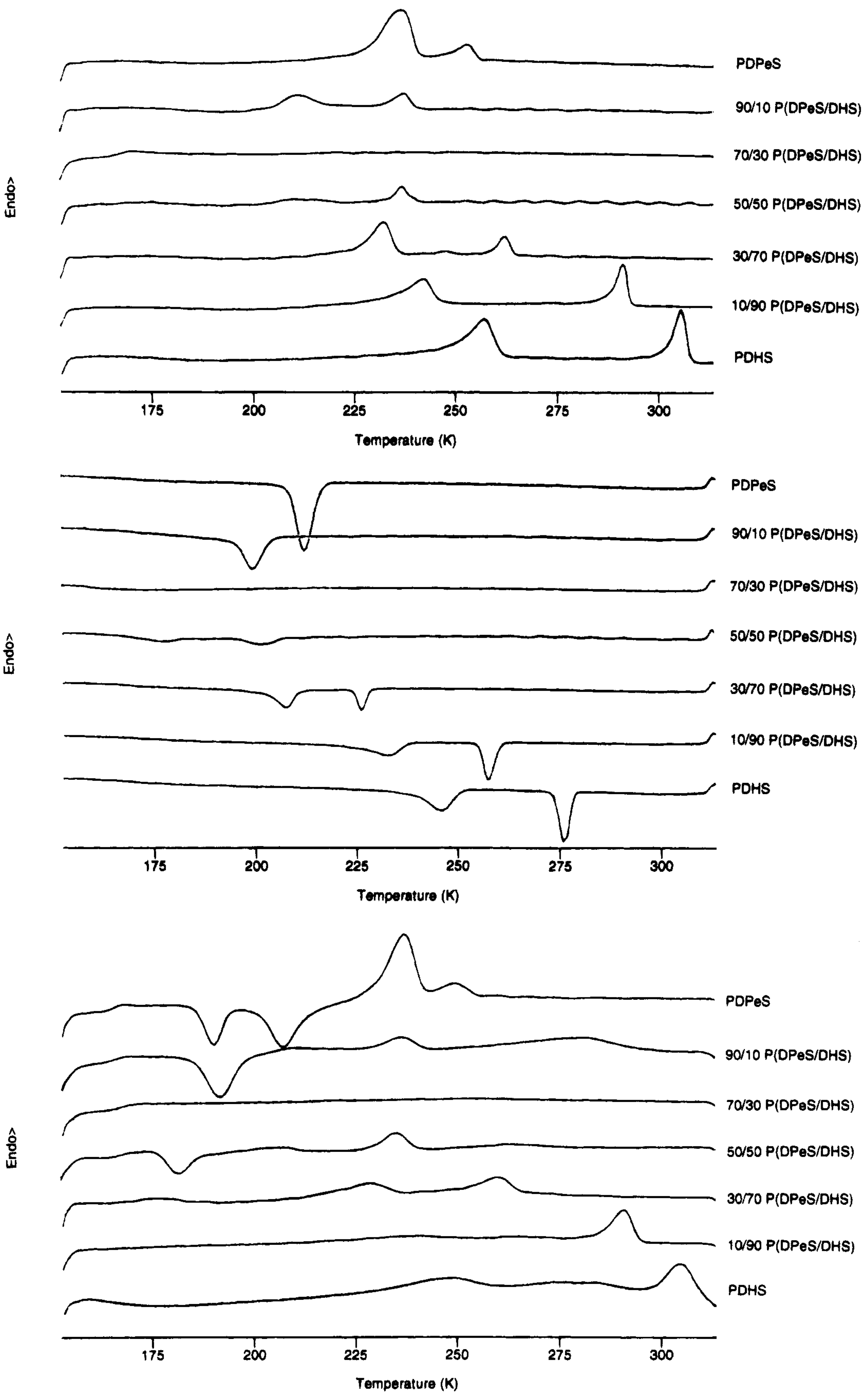

Figure 1. (a, Top) DSC heating scans of copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s after cooling the samples from 323 to 153 K at a rate of 10 K/min (scan rate 10 K/min). (b, Middle) DSC cooling scans of copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s (scan rate 10 K/min). (c, Bottom) DSC heating scans of copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s after quenching the samples from 323 K into liquid nitrogen (scan rate 10 K/min).

in the copolymers. The upfield shift of the isotropic ^{29}Si chemical shift signal upon transition from the fully ordered crystalline phase to the other phases can be explained by an increase in the number of gauche

Table 6. Thermal Transitions of Copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s As Observed in DSC Heating Thermograms (Rate 5 K/min)

% pentyl	DP[a]	T_g[b] (K)	T_{d1} (K)	ΔH_{d1} (kJ/mol)	ΔS_{d1} (J/(K mol))	T_{d2} (K)	ΔH_{d2} (kJ/mol)	ΔS_{d2} (J/(K mol))	T_i[c] (K)
0	6030		246	6.7	27.2	296	5.1	17.2	603
14	3241		229	3.3	14.5	287	3.2	11.1	595
31	2100		224	3.7	16.6	257	1.1	4.3	543
45	1678	167	201	1.2	5.9	231	0.9	4.1	539
65	1823	165	*d*	*d*	*d*	214	1.1	5.1	547
83	2064	165	203	2.5	12.4	231	1.5	6.5	581
100	3535	167	231	9.0	38.8	251	1.9	7.6	603

[a] Based on M_w. [b] After quenching the sample from 323 to 77 K. [c] Disappearance of birefringence after annealing the sample for 10–12 min at 30–50 K below T_i. [d] Recrystallization: $T = 192$ K, $\Delta H = 1.1$ kJ/mol, $\Delta S = 5.5$ J/(K mol).

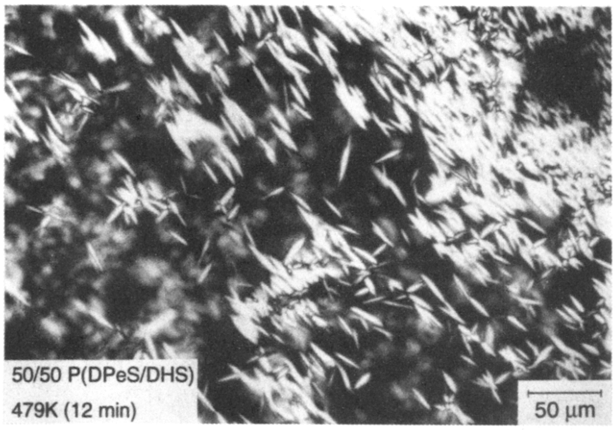

Figure 2. Optical polarizing micrograph of hexagonal columnar 50/50 copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane) after isotropization and 12 min of annealing at 479 K.

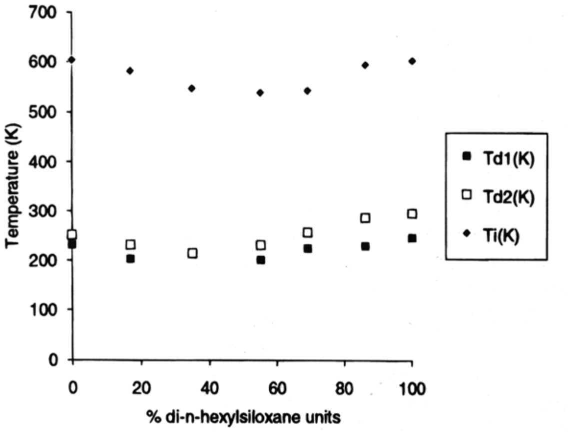

Figure 3. Transition temperatures of copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s.

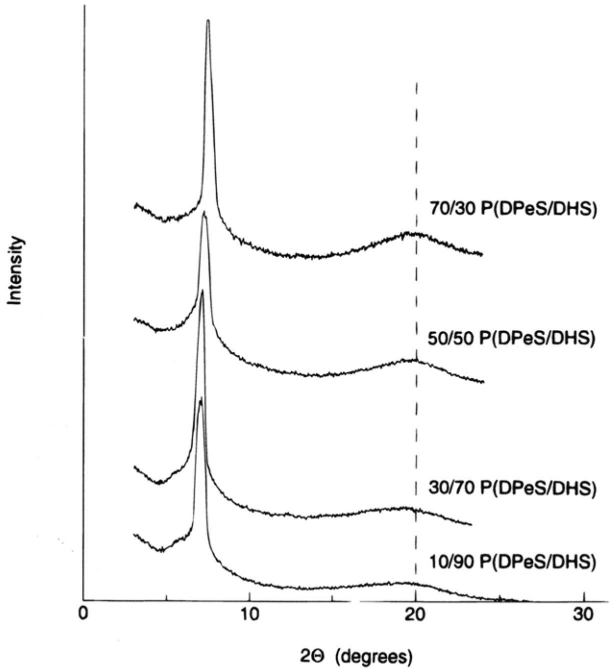

Figure 4. WAXD patterns of hexagonal columnar copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s recorded at 296 K.

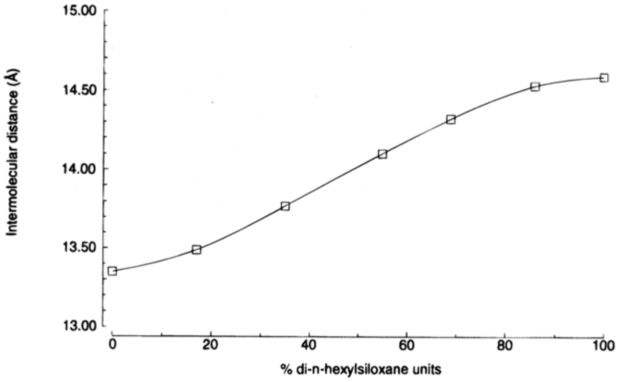

Figure 5. Intermolecular distance in hexagonal columnar copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s at 296 K as a function of the di-*n*-hexylsiloxane content.

conformations, which allows the process of fast exchange conformational interconversion to occur.[18,19] Further heating into the mesophase finally left one sharp signal at −23.8 ppm, which is comparable to the ^{29}Si chemical shift in solution and which points to the liquid-like conformational disordering of the polymer main chain within this 2D ordered phase.

In general, the temperature dependence of the ^{29}Si CSA of 30/70 copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane) (Figure 7) is comparable to that of the corresponding homopolymers.[4] The low-temprature crystalline phase showed a CSA with $\nu_x - \nu_z = 3.5$ kHz. The broadness of the signal demonstrated the rigidity of the polysiloxane main chain in the low-temperature crystalline phase. Transition into the high-temperature crystalline phase yielded a slightly narrower CSA with $\nu_x - \nu_z = 2.9$ kHz, which has become nearly axially symmetric. In line with the observations on the isotropic chemical shifts, the CSA signal is overlapped by the CSA of a fraction of mesomorphic material.

Upon entering the mesophase, a narrow CSA with $\nu_{x'} - \nu_{z'} = 1.1$ kHz remained. The peculiar shape might be caused by overlap of CSA siganls of di-*n*-pentyl- and di-*n*-hexyl-substituted silicon atoms. The stepwise reduction in CSA line width and the reversal in intensities of the components point to the onset of backbone oscillations during the first transition and diffusive rotation of the chain segments around the molecular long axis upon passing the second transition. This behavior is similar to what has been described for the

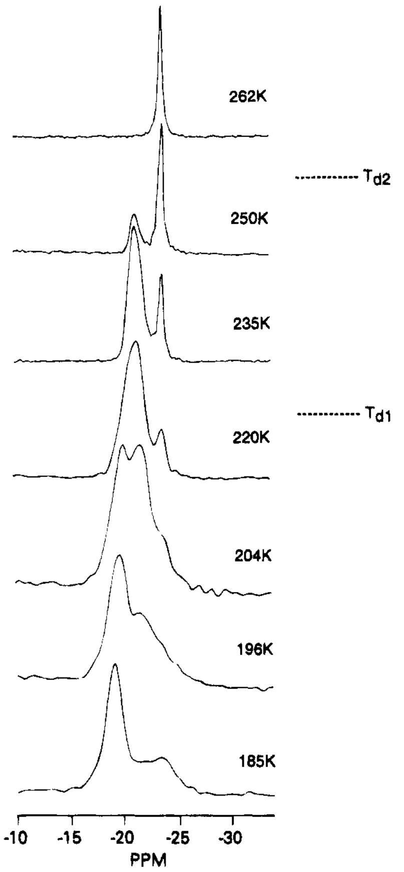

Figure 6. Temperature-dependent ^{29}Si NMR MAS spectra of the 30/70 copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane).

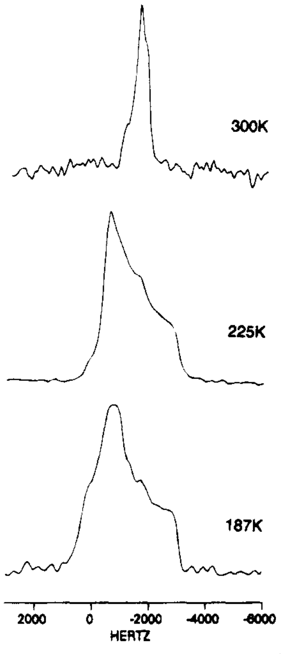

Figure 7. Temperature dependence of the ^{29}Si CSA of 30/70 copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane).

columnar mesophases of the poly(di-*n*-alkylsiloxane) homopolymers.[1-4,20]

Conclusions

High molecular weight random copoly(di-*n*-alkylsiloxane/di-*n*-hexylsiloxane)s have been prepared by cationic ring-opening polymerization of cyclic comonomers using trifluoromethanesulfonic acid as an initiator. The solid-state phase behavior of poly(di-*n*-alkylsiloxane)s appeared to be strongly affected by the presence of comonomeric di-*n*-alkylsiloxane units with different side group lengths. At the example of copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s, it is observed that a difference of one carbon atom can still be accommodated within the 2D-ordered hexagonal columnar phase, even in cases where crystallization into a 3D-ordered structure is hindered, as evidenced by the behavior of 70/30 copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane). However, when the alkyl side groups differed by more than one carbon atom in length, formation of a stable hexagonal columnar mesophase was not displayed anymore, whereas crystallization could still be observed. At a difference of four carbon atoms, crystallization is impeded as well, as demonstrated by the copoly(diethylsiloxane/di-*n*-hexylsiloxane)s containing more than 10% diethylsiloxane units. Thus, increasing the amount of constitutional disorder seems to destabilize both the crystal phase and the columnar mesophase. Whereas crystallization might in some cases be hindered for kinetic reasons and can be induced by supercooling of the isotropic melt, formation of the columnar mesophase is thermodyamically controlled. Extensive disorder within the substitution pattern might render such a large contribution to the total melting entropy that transition into the isotropic melt becomes favorable as opposed to intermediate formation of the 2D-ordered mesophase.

In the case of copoly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s, isotropization temperatures decreased for copolymers of intermediate composition. This was accompanied by a comparable decrease of crystallization temperatures. As a result, the temperature interval ΔT in which the hexagonal columnar mesophase exists retained a relatively constant value of 300°, i.e., similar to the situation for the homopolymers. Destabilization of the crystalline phase due to irregular substitution of the polymer main chain is reflected in decrease transition enthalpies and an increased tendency toward vitrification of the columnar mesophase. This behavior is also observed in the temperature-dependent solid-state MAS ^{29}Si NMR spectra.

Wide-angle X-ray diffraction studies on poly(di-*n*-pentylsiloxane/di-*n*-hexylsiloxane)s confirmed the formation of a hexagonal columnar mesophase. In addition, an S-shaped dependence of the interchain distance on the di-*n*-hexylsiloxane content was observed, demonstrating that side group indentation might occur in the case of copolymers with intermediate composition. The interchain distance displayed by copolymers with 10% of the minor monomeric unit resembled that of the corresponding homopolymers.

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