Controlled Polymerization of Hexa-*n*-alkylcyclotrisiloxanes with Long Alkyl Groups

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ABSTRACT: Hexa-*n*-alkylcyclotrisiloxanes with side chains ranging from butyl up to decyl were polymerized anionically with cryptated lithium as the counterion. The polymerizations usually yielded polymers with low polydispersity, demonstrating the presence of a single growing species and the successful breaking up of aggregates. Formation of bimodal molecular weight distributions in the polymerization of the cyclic trimers containing heptyl up to decyl side chains can be explained by the presence of traces of siloxanediol, leading to some chains growing at both ends.

Introduction

The use of cryptated lithium as a counterion in the anionic polymerization of hexamethylcyclotrisiloxane (D_3^{Me}),[1] hexaethylcyclotrisiloxane (D_3^{Et}),[2−4] and hexapropylcyclotrisiloxane (D_3^{Pr})[3,4] has proven to be a successful approach to the synthesis of well-defined polysiloxanes. A lithium silanolate endgroup is formed in situ by addition of an organolithium compound to the monomer. In nonpolar media this silanolate is unreactive and polymerization starts only upon addition of a lithium-complexing compound, e.g., the cryptand [211]. This system provides a much better defined initiation step than possible with the often used alkali metal hydroxides.[5] The latter dissolve only slowly and at elevated temperatures and form a silanol endgroup, which is capable of splitting off water upon condensation with other silanol groups.[6]

Increasing the length of the side chain from methyl to ethyl has been shown to cause a strong decrease in the propagation rate.[2,3] Furthermore, siloxane polymerizations are hampered by the existence of a propagation−depropagation equilibrium between linear chains and rings containing four or more siloxane units.[5] Upon increasing side chain length, the equilibrium concentrations of the latter increase strongly.[7] Due to their ring strain, polymerization of the cyclic trimers offers the possibility of kinetic control. The enhanced reactivity of the siloxane bond in these monomers causes chain propagation to proceed much faster than equilibration,[5] and the amount of cyclic byproducts can be strongly reduced by quenching the polymerization well below 100% monomer conversion.

Poly(di-*n*-alkylsiloxane)s with butyl, pentyl, and hexyl side chains have been synthesized by anionic polymerization of the corresponding cylic trimers, using CsOH as initiator.[8−10] Hexa-*n*-alkylcyclotrisiloxanes carrying heptyl up to decyl side chains were polymerized cationically, using trifluoromethanesulfonic acid as the initiator.[8,9] In all cases high molecular weight polymers were obtained, which, however, had to be fractionated in order to obtain acceptable molecular weight distributions (1.2−2.0). Due to the complicated mechanism of the cationic polymerization, showing many side reactions,[11] and the troublesome dosing of the crystalline initiator (CsOH) in the anionic polymerization, molecular weight control was difficult to achieve.

The present work regards utilization of the cryptated lithium (Li^+/[211]) system for the anionic polymerization of hexa-*n*-alkylcyclotrisiloxanes with butyl up to decyl side chains.

Experimental Section

Materials. Hexa-*n*-alkylcyclotrisiloxane (D_3^R) monomers were prepared as described before.[9] D_3^{Bu}, D_3^{Pe}, and D_3^{Hex} were dried by vacuum distillation from CaH_2. Due to their high boiling points, the monomers with longer side chains had to be dried azeotropically with toluene/$Mg(C_4H_9)_2$. The cryptand [211] (Merck, 98%) was distilled under high-vacuum conditions, using a quartz apparatus.[3] The ligand was obtained as a colorless liquid, which was dried azeotropically with toluene/$Mg(C_4H_9)_2$, dissolved in absolute toluene, and stored under nitrogen in a quartz flask. The initiator lithium *sec*-butyldimethylsilanolate (*s*-BuSi(Me_2)OLi) was prepared by reacting *s*-BuLi (Aldrich; 1.3 M in cyclohexane) with 0.33 equiv hexamethylcyclotrisiloxane (Aldrich; >98%, distilled from CaH_2).[12] Chlorotrimethylsilane (ABCR; 99.9%) was used as received.

Polymerizations. Polymerizations were performed on a 1 g scale in bulk in thoroughly cleaned and dried 10 mL flasks equipped with a Teflon stirring bar under a nitrogen atmosphere containing less than 1 ppm of O_2 and H_2O. After subsequent addition of the initiator and cryptand solutions to the monomer, the reaction mixture was heated to 60 °C and stirred at that temperature for several hours, during which a gradual increase in viscosity could be observed. Polymerizations were terminated with chlorotrimethylsilane, and polymers were obtained by repeated precipitation in hot ethanol (PDBuS and PDPeS) or hot 2-propanol (PDHexS−PDDecS). The low molecular weight fraction consisting of residual monomer and larger rings was recovered by evaporation of the alcohol and was analyzed by either GC or ^{29}Si NMR.

Methods. Molecular weights and molecular weight distributions were obtained from GPC. The setup consisted of Waters μ-Styragel columns with pore sizes of 10^5, 10^4, 10^3, and 500 Å. Sample detection was performed by a Waters 410 differential refractometer and a Wyatt Dawn DSP-F laser photometer, measuring light scattering at 18 angles between 15.6° and 144.5° and allowing the determination of absolute values for M_w. THF was used as the eluent, and the setup was calibrated with narrow polystyrene samples. In the case of bimodal molecular weight distributions, the RI signal was deconvoluted by fitting two Gaussian curves.

^{29}Si NMR spectra were recorded in $CDCl_3$ at 300 K on a Bruker AMX500 spectrometer at 99.4 MHz. TMS was used

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Table 1. ^{29}Si Chemical Shifts of Cyclo-*n*-alkylsiloxanes (ppm, relative to TMS)

R	D_3^R	D_4^R	D_5^R
hexyl	−10.6	−21.9	−24.7
heptyl	−10.6	−21.9	−24.7
octyl	−10.7	−21.9	−24.6
nonyl	−10.6	−21.9	−24.7
decyl	−10.6	−21.9	−24.4

as internal standard, and delay times of 60 s were chosen between successive scans in order to ensure near to complete relaxation of the ^{29}Si nuclei. Table 1 lists the chemical shifts of the di-*n*-alkylsiloxane rings.

Results and Discussion

Several poly(di-*n*-alkylsiloxane)s were synthesized by anionic ring-opening polymerization of their corresponding cyclic trimers (D_3^R) in bulk. Polymerizations were initiated by addition of lithium *sec*-butyldimethylsilanolate (*s*-BuSi(Me$_2$)OLi) in combination with the lithium complexing cryptand [211]. Table 2 lists a number of representative results. After precipitation, the low molecular weight fraction, consisting of residual monomer and larger rings formed by backbiting reactions, was recovered by evaporation of the alcohol and analyzed by either GC or ^{29}Si NMR (Table 3). Comparing the obtained molecular weights with the calculated values shows that the Li$^+$/[211] system offers good control in the polymerizations of D_3^{Bu} (runs 1 and 2). When only the low molecular weight peak is taken into account, the same holds for the polymerizations of D_3^{Hep} (runs 7 and 8). At increasing conversion (compare polymerizations 7−9) or increasing side chain length (compare polymerizations 2, 6, 8, 9, 11 and 3, 5, 7, 10, respectively), the amount of backbiting increases. Comparison of entries 5 with 6 and 3 with 4 in Table 2 hints at the existence of a molecular weight-limiting side reaction. Such a side reaction has also been found to hamper the polymerization of hexaethylcyclotrisiloxane with the Li$^+$/[211] system,[2] where it was particulary important at high monomer/initiator ratios. The mechanism of this side reaction is not known yet.

The molecular weight distributions for PDHepS, PDOctS, and PDNonS are bimodal, with an increasing fraction of high molecular weight polymer on going from heptyl to nonyl side chains. This is illustrated in Figure 1 for a PDHepS and a PDNonS sample, respectively. Bimodality has also been reported for the polymerization of hexamethylcyclotrisiloxane with a Li$^+$ counterion promoted by HMPT.[13] Variation of the rate constant caused by changes in aggregate molecularity of the living ends was proposed as an explanation for this phenomenon. However, the use of [211] as a lithium-complexing compound usually suppresses aggregation,[1] although the effect of the alkyl group in D_3^R is unknown. Analysis of the GPC light scattering signals revealed that the high molecular weight fractions have 2 times the molecular weight of the low molecular weight fractions. This can be explained by the presence of some chains that grow at both ends. Water is known to cause this effect,[14,15] but since the monomers are hydrophobic and have been carefully dried before polymerization, the bifunctional growing chains more likely stem from the

Table 2. Results of D_3^R Polymerizations in Bulk at 60 °C Using Li$^+$/[211] as Counterion

entry	R	$[D_3^R]_0$/[−SiOLi]	time (h)	yield (%)	M_n (calcd)[a] (10^3 g/mol)	M_n[b] (10^3 g/mol)	M_w[b] (10^3 g/mol)	M_w/M_n[b]	M_w[c] (10^3 g/mol)	d*n*/d*c*[c] (mL/g)
1	butyl	628	48[d]	62	186	176	194	1.10	199 ± 6	0.052
2	butyl	630	5.5	48	142	141	149	1.06	150 ± 8	0.053
3	pentyl	500	16	84	235	128	161	1.26	174 ± 10	0.058
4	pentyl	826	20[e]	83	383	118	170	1.44	209 ± 10	0.052
5	hexyl	448	20	88	254	173	198	1.14	239 ± 10	0.060
6	hexyl	1290	32	54	541	176	206	1.17	297 ± 30	0.063
7	heptyl	392	14	90	257	peak 1, 93 wt %	246	1.04	92 wt %, 241 ± 4	0.058
						peak 2, 7 wt %	363	1.10	8 wt %, 529 ± 4	
8	heptyl	399	8.2	51	147	peak 1, 85 wt %	127	1.04	85 wt %, 135 ± 9	0.061
						peak 2, 15 wt %	199	1.11	15 wt %, 251 ± 10	
9	heptyl	423	8.5	51	157	peak 1, 77 wt %	127	1.04	80 wt %, 154 ± 8	0.059
						peak 2, 23 wt %	203	1.08	20 wt %, 293 ± 10	
10	octyl	353	20	89	254	peak 1, 75 wt %	175	1.05	76 wt %, 226 ± 9	0.064
						peak 2, 25 wt %	321	1.18	24 wt %, 529 ± 30	
11	nonyl	253	11	53	148	peak 1, 75 wt %	89	1.05	72 wt %, 88 ± 4	0.065
						peak 2, 25 wt %	150	1.09	28 wt %, 171 ± 4	
12	decyl	330	46	68	219	15.8	21.1	1.33		0.065

[a] Calculated from isolated yield and monomer/initiator ratio. [b] From GPC in THF, polystyrene calibration; in the case of two peaks, the values for M_w and M_w/M_n are obtained after deconvolution of the overlapping peaks. [c] From GPC in THF, on-line light scattering. [d] At 26 °C. [e] At 80 °C.

Table 3. Compositions of the Reaction Mixtures after Termination

entry	R	$[D_3^R]_0$/[−SiOLi]	polymer (wt %)	method	D_3^R (wt %)	D_4^R (wt %)	D_5^R (wt %)
1	butyl	628	62	GC	37	1.4	
2	butyl	630	48	GC	51	1.3	
3	pentyl	500	84	GC	12	4.1	0.1
4	pentyl	826	83	GC	5.8	11	0.5
5	hexyl	448	88	GC	7.4	4.4	0.2
				^{29}Si NMR	7.1	4.7	0.2
6	hexyl	1290	54	GC	43	2.6	0.05
7	heptyl	392	90	^{29}Si NMR	0.8	8.3	0.9
8	heptyl	399	51	GC	46	2.9	
9	heptyl	423	51	GC	46	3.4	
10	octyl	353	89	^{29}Si NMR	4.2	5.4	1.4
11	nonyl	253	53	^{29}Si NMR	36	4.2	6.6
12	decyl	330	68	^{29}Si NMR	2.6	27	2.9

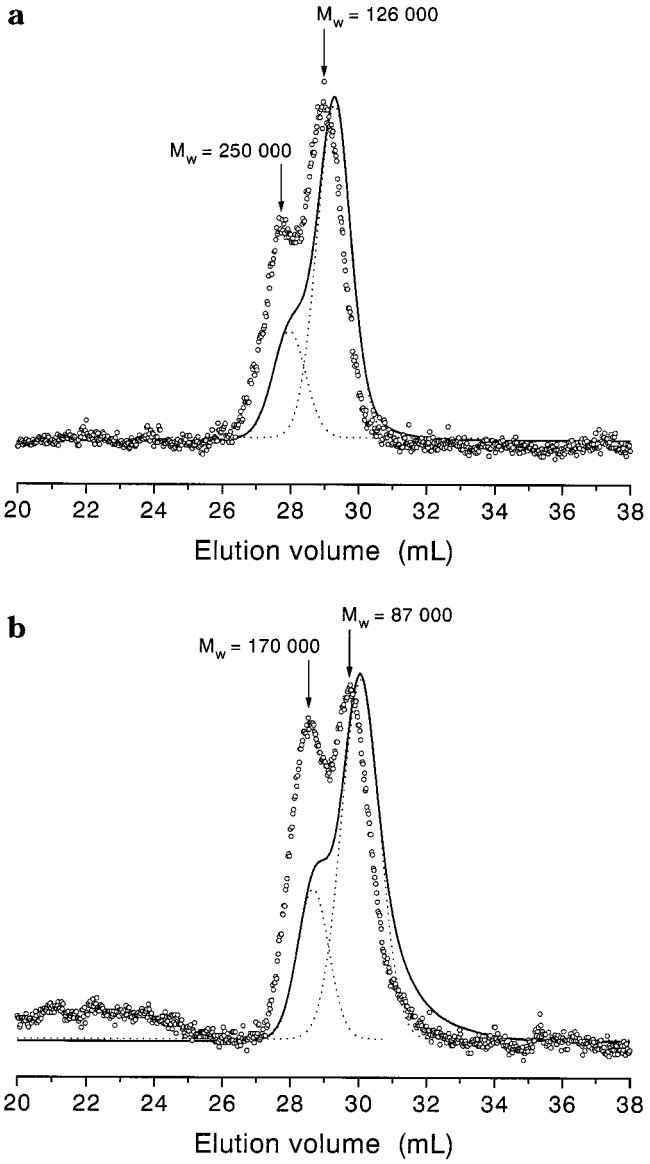

Figure 1. GPC elugrams (○, light scattering signal at 90°; — RI signal) for (a) PDHepS (entry 9) and (b) PDNonS (entry 11). The dotted lines indicate the deconvolution of the RI signal.

presence of siloxanediols (assuming that the silanol condensation is slower than the polymerization). The hexa-*n*-alkylcyclotrisiloxane monomers, which were synthesized by condensation of the corresponding dichlorosilanes and purified by repeated recrystallization from 2-propanol,[9] may still contain some $HO[Si(R_2)O]_nH$ (n = 1 or 2). We have found these disilanols, even after high-vacuum distillation at ca. 200 °C, as side products in the synthesis of similar monomers containing sterically hindered pentyl side chains. The amount of disilanols may be expected to increase upon increasing steric hindrance around the silicon atom, and their removal by recrystallization may be expected to be less efficient if the side chains become longer (i.e., the molecule becomes more apolar). At a monomer/initiator ratio of 400, contamination of the monomer with 0.05 mol % siloxanediol will cause 30 wt % high molecular weight fraction. The silanol groups can be considered as dormant living centers, which are in equilibrium with the silanolate chain ends. The silanol−silanolate exchange has been shown to be extremely fast,[16] and therefore, mono- and bifunctional growing chains both show a narrow molecular weight distribution. In the polymerization of hexa(decyl)cyclotrisiloxane, molecular weight control was poor. This may be caused by extensive transfer, due to the presence of a relatively high amount of silanol units.

In conclusion, it can be stated that the anionic polymerization of hexa-*n*-alkylcyclotrisiloxanes with side chains ranging from butyl up to decyl using cryptated lithium as the counterion usually yields polymers with low polydispersity, particulary for D_3^R, where R = butyl, pentyl, or hexyl.

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