Kinetics and Thermodynamics of the Ring Opening Reaction of Hexamethylcyclotrisiloxane

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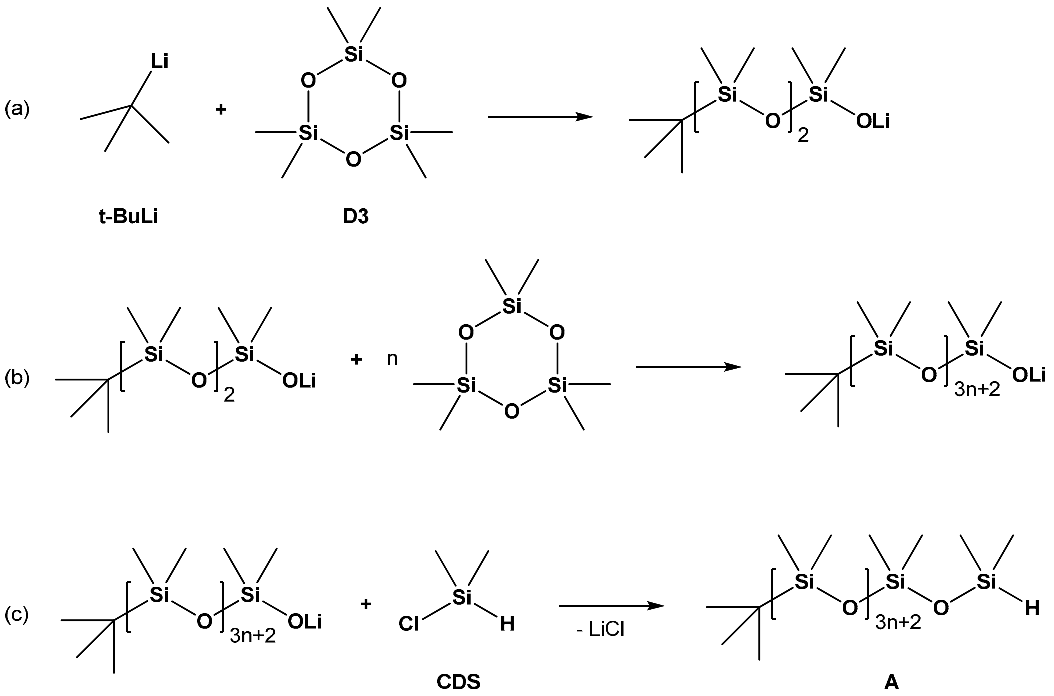
The kinetics and the thermodynamic properties of the ring opening reaction of hexamethylcyclotrisiloxane (D3) were determined. The reaction obeys second order kinetics and is highly exothermic. Moreover, the reaction is irreversible and no side products were detected. The lithium silanolate which is produced in this reaction efficiently initiates the ring opening polymerization (ROP) of D3. This anionic polymerization reaction can be applied in synthesis of oligo- and polysiloxanes with a narrow molecular weight distribution. The reaction is quenched with chlorodimethylsilane (CDS) by forming endcapped monohydrido substituted oligo- or polysiloxanes.

Introduction

Linear polydimethylsiloxanes have high industrial importance. These substances are either produced from monomers containing one silicon atom (e.g. methanolysis of dichlorodimethylsilane) or by cationic or anionic ring opening polymerization (ROP) of cyclic oligosiloxanes (e.g. octamethylcyclotetrasiloxane)[1]. Industrial scale polysiloxanes mostly carry identical end groups on both chain ends. Monofunctional oligo- and polysiloxanes of type A (Scheme 1c) are interesting starting materials for many products[2]. In order to get well defined physical and chemical properties a narrow molecular weight distribution[3] is required. The anionic ring opening polymerization of hexamethylcyclotrisiloxane (D3) (Scheme 1) is a promising route for the synthesis of monofunctional oligo- and polysiloxanes[3-5] with low dispersion. This project deals with the synthesis of these substances in a micro-scale continuous plug flow reactor (CPFR) under quasi-isothermal conditions. The ROP is efficiently initiated by *tert*-butyllithium (t-BuLi) (Scheme 1a). Compared with the importance of this reaction, only few kinetic[6,7] and thermodynamic data is available for this specific type of reaction. For successful process development, this profound data has to be determined. Our investigation focused on the synthesis of monohydrido substituted oligo- and polysiloxanes. The first step of the anionic ROP, the initiation reaction of D3 with t-BuLi, is discussed in detail.

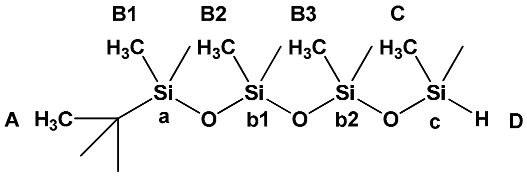


Scheme 1. Ring opening polymerization of D3 initiated by t-BuLi and terminated by chlorodimethylsilane (CDS): (a) Initiation reaction; (b) Propagation reaction; (c) Termination reaction

Experimental Part

Chemicals and preparation. Hexamethylcyclotrisiloxane (D3) was received from GE Bayer Silicones in a liquid mixture of cyclic oligosiloxanes. This mixture was distilled several times; purity was controlled with ^{1}H and ^{29}Si-INEPT spectroscopy. Pure D3 was dried over calciumhydride prior to use. *tert*-Butyllithium solution (1.6 M in pentane) is a commercial product (Acros Organics) and was used as received. The concentration and stability of the solution was controlled by titration following Gilman [8, 9]. Chlorodimethylsilane is a commercial product (ABCR, 95 %); the received solution was distilled under nitrogen atmosphere. Quality was controlled with ^{1}H and ^{29}Si-INEPT spectroscopy. THF (Acros) was dried with standard methods (innovative technology, inc.). Chloroform (Fisher Scientific, Analytical Reagent Grade) was pre-dried with calciumchloride, heated to reflux with phosphorouspentoxide under nitrogen atmosphere and distilled off the flask.

Synthesis of 1-*tert*-Butyl-7-hydrido-1,1,3,3,5,5,7,7-octamethyltetrasiloxane. In a flame-dried Schlenk flask, 0.20 g of D3 (0.90 mmol), dissolved in 4.0 mL THF, was reacted with 0.56 mL of the t-BuLi solution (0.90 mmol) for 1 h at 0°C. To stop the reaction, 0.12 mL CDS (1.12 mmol) was added dropwise. The ice bath was removed after 15 min and when room temperature was reached the solvent was removed. 3.0 mL pentane was added to the residue and the resulting solution was filtered. Pentane was evaporated and the product, a colorless liquid, was characterized by ^{1}H and ^{29}Si-INEPT NMR spectroscopy (Figure 1 and Figure 2).



Scheme 2: Structure of 1-*tert*-butyl-7-hydrido-1,1,3,3,5,5,7,7-octamethyltetrasiloxane

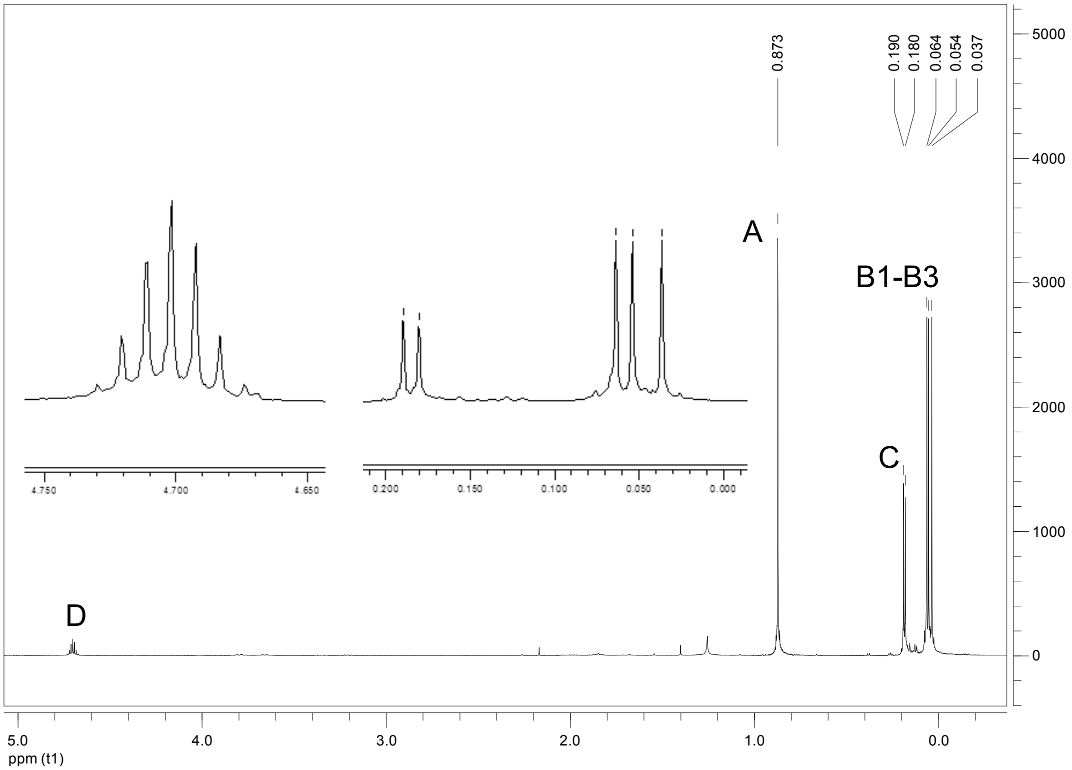


Figure 1: ^{1}H NMR (300 MHz) spectrum of 1-*tert*-butyl-7-hydrido-1,1,3,3,5,5,7,7-octamethyltetrasiloxane in $CDCl_3$

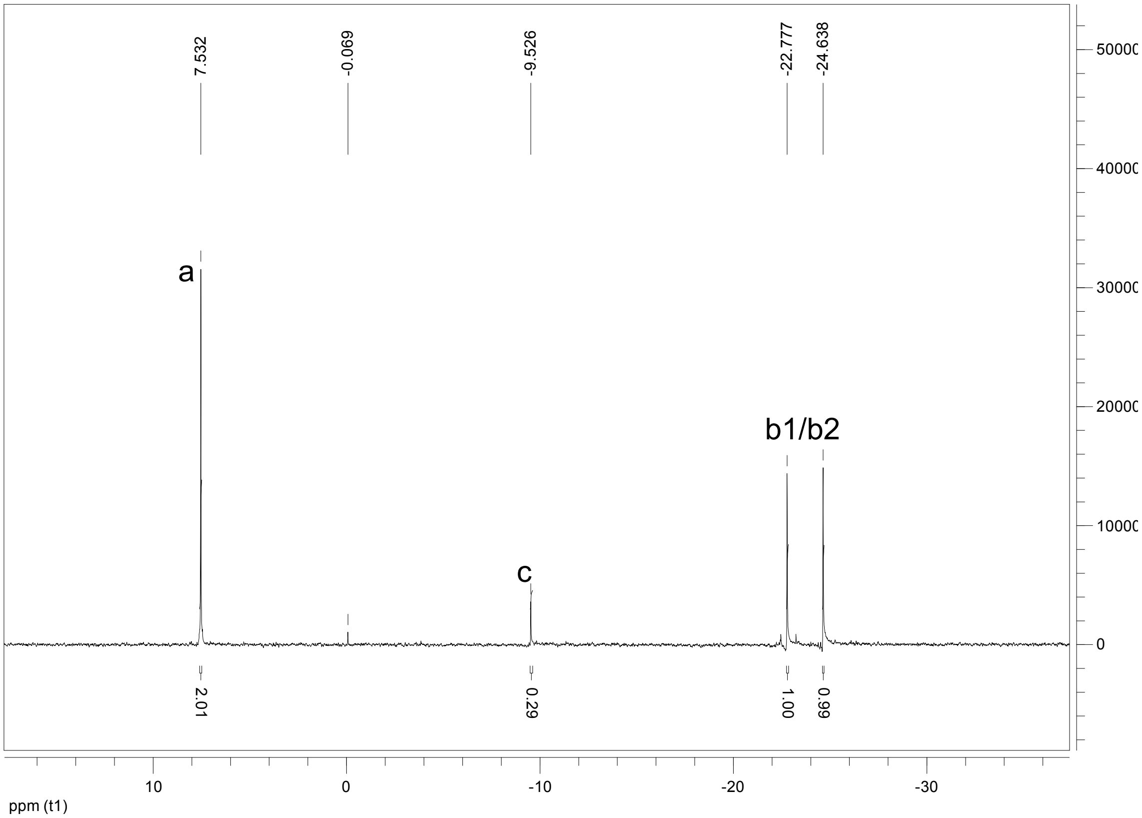


Figure 2: ^{29}Si-INEPT NMR (300 MHz) spectrum of 1-*tert*-butyl-7-hydrido-1,1,3,3,5,5,7,7-octamethyltetrasiloxane in $CDCl_3$

^{1}H NMR ($CDCl_3$): δ = 0.037 – 0.064 (3s, ($C\underline{H}_3)_2$SiO), δ = 0.0180 – 0.0190 (d, ($C\underline{H}_3)_2$SiH), δ = 0.873 (s, ($C\underline{H}_3)_3$C), δ = 0.190, δ = 4.674 – 4.730 (m, Si$\underline{H}$)

^{29}Si-INEPT NMR ($CDCl_3$): δ = -24.637 – -22.776 (2s, O$\underline{Si}$O), δ = -9.525 (s, O$\underline{Si}$H), δ = 7.533 (s, Bu$^t\underline{Si}$O), δ = -0.069 (s, SiH oxidation by-product)

Kinetic studies. All kinetics experiments were carried out in the dry box under nitrogen atmosphere. The temperature of the reaction solution was recorded online during the experiments. A heptane cooling bath was used to maintain isothermal conditions in the reaction vessel. The cooling bath was cooled with a copper heat exchanger connected to a cryostatic temperature controller. Experiments were run in a temperature window of θ = -40°C and θ = -70°C.

0.10 g D3 (0.45 mmol) dissolved in 8.0 mL THF was cooled to the desired reaction temperature. 0.28 mL of the t-BuLi solution (0.45 mmol) was slowly added to the reaction vessel. The resulting temperature increase never exceeded more than 2 K.

A quench solution consisting of 0.31 mL CDS dissolved in 20.0 mL $CHCl_3$ was prepared. 4.0 mL of this quench solution (49.7 mmol $CHCl_3$, 0.56 mmol CDS) was added at desired reaction time to instantly stop the reaction. This experiment was repeated multiple times to get the conversion curve of D3. ^{1}H NMR spectroscopy was used to get the ratio between reacted and unreacted D3.

Thermodynamic studies. Experiments were carried out in a Dewar vessel under adiabatic conditions. The temperature of the solution was recorded online during the experiments. 3.00 g D3 (13.5 mmol) were dissolved in 150.0 mL cooled THF. 8.4 mL of the t-BuLi solution (13.5 mmol) was added slowly. After the reaction was completed 1.5 mL CDS (13.5 mmol) was added. Then, ^{1}H and ^{29}Si-INEPT NMR spectroscopy was used to check whether conversion was completed.

Results and Discussion

During the initiation reaction of D3 with t-BuLi no side product formation was detected. The reaction is irreversible, resulting in a complete conversion of D3 to the corresponding lithium-silanolate. The reaction obeys second order kinetics.

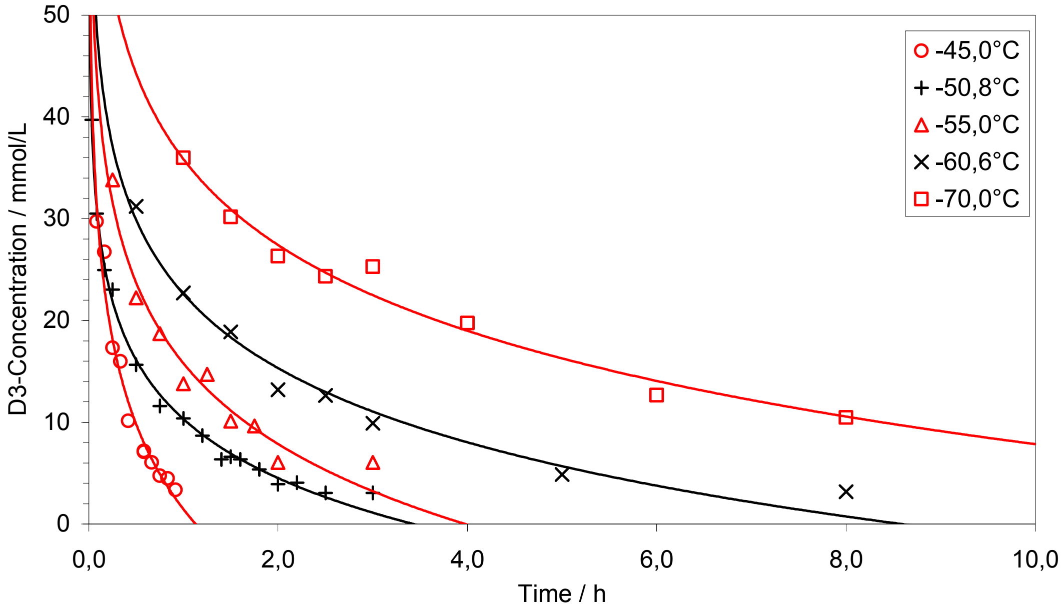


Figure 3. Conversion curves of D3 with t-BuLi in THF at various temperatures

From the data of Figure 3 the Arrhenius parameters were calculated (Figure 4).

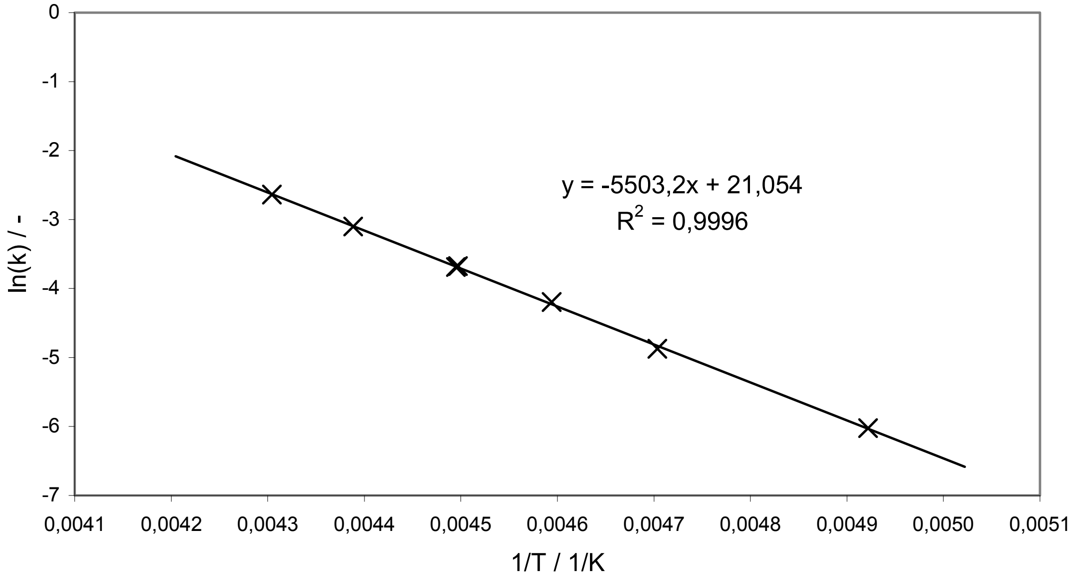


Figure 4. Arrhenius plot of the initiation reaction of D3 with t-BuLi in THF

The activation energy, E_A, was found to be 45.8 kJ mol^{-1} and the frequency factor, k_0, equals $1.39 \cdot 10^9$ L mol^{-1} s^{-1}. The enthalpy of reaction, $\Delta_R H$, was found to be -206.6 ± 5.4 kJ mol^{-1}. With this data it was possible to predict adiabatic conversion of D3. Figure 5 shows the comparison of the simulated and the experimentally obtained temperature (conversion) curve.

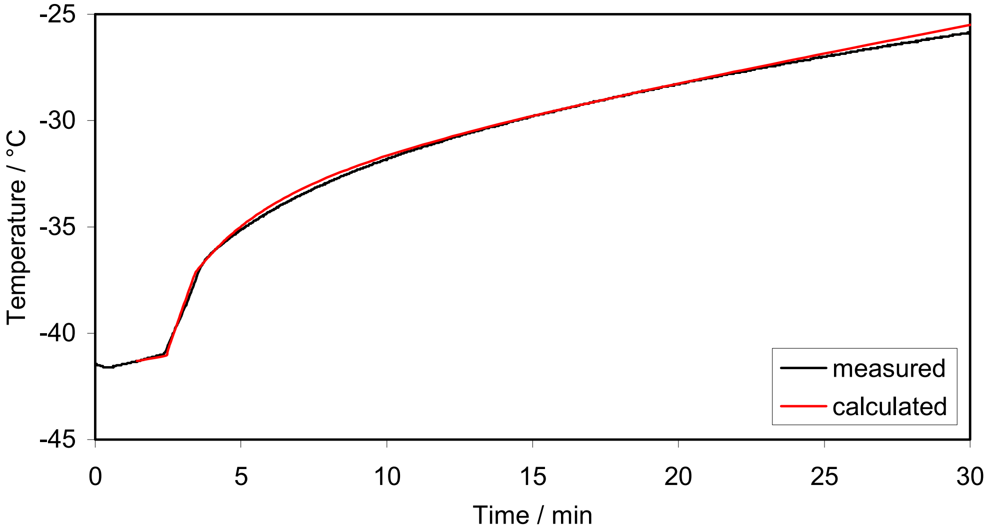


Figure 5. Comparison of the simulated and the experimentally obtained temperature curve of the initiation reaction of D3 with t-BuLi

The kinetic experiments were repeated with octamethylcyclotetrasiloxane (D4) instead of D3 in a temperature window of θ = -50°C and θ = 20°C for a maximum reaction time of 1 h. Opposite to D3, no conversion of D4 to the corresponding linear lithium-silanolate was detected. Reason for the different reactivity is the large difference in the ring strain[10], which is 10.5 kJ mole^{-1} for D3 and 1.0 kJ mole^{-1} for D4.

Summary

First polymerization reactions showed that the ROP is efficiently initiated by t-BuLi. Kinetics as well as thermodynamics of the initiation step was quantified. Data accuracy was tested with simulation and experimental validation of adiabatic reaction conditions. The ROP reaction is predicted to be selective for D3 in mixtures with other cyclic oligosiloxanes. First experiments of D3-D4-mixtures in THF approved this assumption. If and how kinetics of the D3 ROP is influenced by other cyclic oligosiloxanes is subject of present investigations. Main target is the development of a continuous plug flow reactor (CPFR) which is fed with the received cyclo-oligosiloxane mixture (see *Chemicals and Preparation*) without prior purification.

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