

Branched siloxanes as possible new heat transfer fluids for application in parabolic through solar thermal power plants



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ABSTRACT

Concentrating solar power is a promising technique for future energy supply. The currently used heat transfer fluid in those power plants is a eutectic mixture of biphenyl and diphenylether. This mixture limits the maximum operating temperature of a concentration solar power plant due to occurring degradation. Polysiloxanes are a promising substitution as heat transfer fluid due to their good resistance towards high temperatures. Nevertheless, those polymers are subjected to a thermally induced equilibration reaction which leads to an alternation in the physical properties. In our study we could demonstrate, based on chosen model compounds, that branched siloxanes have a remarkable resistance against thermal equilibration reaction.

1. Introduction

In consideration of global warming and decreasing fossil resources, it is necessary for future energy supply to reduce the amount of fossil energy and to replace it with renewable, clean and sustainable energy sources. Of all possible renewable energy sources, the sun is by far the most abundant [1,2]. A promising technology for utilizing the solar radiation for energy production is concentrating solar thermal power (CSP). Even though with a worldwide capacity of approximately 4 GW in 2014 the amount of electricity produced by CSP is very small compared to 150 GW capacity delivered by photovoltaic [3].

A CSP power plant consists of large mirrors focusing the sunlight either on a linear (technologies: Parabolic Through, Linear Fresnel) or point receiver (technologies: Solar Tower, Parabolic Dish) through which a heat transfer fluid (HTF) circulates. The heated HTF is transferred to the power block site, where superheated steam is generated at a heat exchanger. The steam is then utilized to power a turbine that produces electricity. In addition, CSP plants can be equipped with a thermal energy storage option which provides a CSP plant to generate electricity even at night. This option makes a CSP plant applicable for base load operation. Furthermore, it increases the solar electricity production of the CSP plant and reduces therefore the average costs of generating a kilowatt-hour of electricity [3–5].

With about 95% [6] market share the most widely and commercially proven type of CSP plants are those using line focusing parabolic trough (PT) collectors to heat the HTF [7,8]. The commonly used HTF

in such a PT solar power plant is a eutectic mixture of the organic compounds biphenyl and diphenyloxide [8,9]. This organic HTF limits the operation temperature of the solar thermal power plant to a maximum of ca. 400 °C [8–10], since above this temperature degradation reactions occur [9].

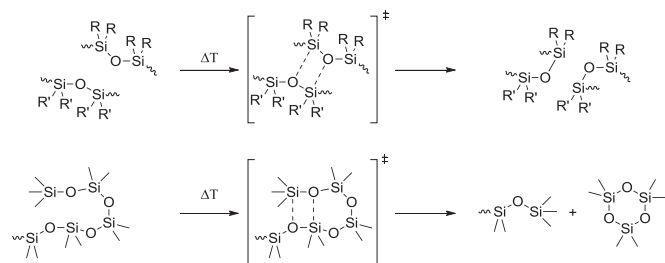
Using a more temperature stable HTF the operating temperature could be raised, which would lead to a significant higher efficiency of the solar thermal power [5,11]. Current ideas comprise the use of binary or ternary mixtures of nitrate salts as HTF. Those eutectic mixtures would allow operating temperatures of 500 °C or higher [10]. Nevertheless, those nitrate salt mixtures face the problem of freezing inside of the tubing since their melting points vary from 65 °C to 220 °C [10,12]. Therefore freeze protection has to be considered when planning and constructing a new CSP plant [10]. Furthermore, it has to be taken into account that the use of nitrate salts at elevated temperatures forces corrosion of the piping [10,12].

A possible alternative for the currently used eutectic mixture of diphenyl and biphenyloxide could be the well-known substance class of siloxanes. Polysiloxanes are polymers built up by a Si-O-Si backbone with organic residues attached to the silicon atoms. Those polymers are characterized by their very useful chemical and mechanical properties, low toxicity and their exceptional thermal stability up to 350 °C in oxygen, acid and base free conditions [13–15].

The good temperature resistance of linear polysiloxanes, in a non-oxidative atmosphere, qualifies this substance class for application as HTF in CSPs. Nevertheless, there are some drawbacks. Several pub-

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Scheme 1. Top: Thermal induced redistribution reaction (random scission) via a four-centered transition state as an intermolecular reaction. Bottom: Thermal induced redistribution reaction (random scission) via a four-centered transition state as an intramolecular reaction.

lications report that the molecular weight distribution of linear and trimethylsilyl terminated polysiloxanes will change if they are exposed to high temperatures in inert and dry conditions. Small cyclic siloxane oligomers are formed due to a thermally induced equilibration reaction. Thomas and Kendrick [16,17] proposed in 1969 the so called “random scission” mechanism for this observation. At elevated temperatures the siloxane bonds rearrange via a four-centered transition state (Scheme 1, top). This reaction can either occur intermolecular between two polysiloxane chains or intramolecular. In the latter case, a chain end flips back due to the high flexibility of the Si-O bond (Scheme 1, bottom) [18]. This allows then the formation of smaller cyclic siloxanes [19,20]. The occurrence of such equilibration reactions would have a negative impact on the nature of the HTF. So, the formation of low molecular compounds might change the physical properties of the liquid such as vapor pressure or viscosity. This would make a continuous operation of a plant more difficult.

A further literature known degradation mechanism of linear polysiloxanes at elevated temperatures is the “unzipping” mechanism. Hereby a silanol or hydroxyalkyl terminated polysiloxane depolymerizes by back-biting of the polymer chain. This leads to exchange or rearrangement reactions and formation of oligomeric cyclic siloxanes [21]. This kind of depolymerization reaction does not occur within trimethylsilyl endcapped polysiloxanes. An additional factor for the stability of polysiloxanes is their purity. Studies showed that small amounts of ionic or polar impurities have a negative influence on the thermal stability of polysiloxanes [22–25]. Therefore impurities need to be avoided.

Our intention was to develop a new high-temperature HTF for application in solar thermal power plants. One of the major requirements of such a HTF is the long-term consistency of physical properties such as vapor pressure or viscosity. Furthermore, it is of importance that a new HTF does not promote corrosion of piping or valves. We decided to explore if there is a way to improve the thermal stability of linear polysiloxanes. Our idea was to test if changes in the structure of the siloxanes are able to suppress the thermally induced equilibration mechanisms as observed for linear polysiloxanes (Scheme 1). For these reasons, we especially examined selected oligomeric model compounds consisting of **TM**- and **QM**-units regarding their stability towards random scission. Tris(trimethylsilyloxy) methylsilane (**TM₃**), 1,1,3,3-tetrakis(trimethylsilyloxy)- 1,3-dimethyldisiloxane (**T₂M₄**), 1,1,3,3-tetrakis(1,1,1,3,5,5,5-heptamethyltrisiloxane)-1,3-dimethyldisiloxane (**T₆M₈**), 1,1,1,3,3-pentakis(trimethylsilyloxy)-3-methyldisiloxane (**QTM₅**), tetrakis(trimethylsilyloxy)silane (**QM₄**) and hexakis(trimethylsilyloxy)disiloxane (**Q₂M₆**) were chosen as model compounds. An overview of the selected model compounds is given in Fig. 1.

Due to the volatility of these compounds the thermal analysis via TGA was not applicable. Therefore, we sealed the model compounds under vacuum in borosilicate glass ampoules and tempered them at 400 °C for several hours. Afterwards the tempered siloxanes were analyzed by NMR spectroscopy and gas chromatography.

2. Experimental section

According to the conventional silicone nomenclature the functional units are abbreviated as follows: **M**-unit $\text{Me}_3\text{SiO}_{1/2}$; **D**-unit $\text{Me}_2\text{SiO}_{2/2}$; **T**-unit $\text{MeSiO}_{3/2}$; **Q**-unit $\text{SiO}_{4/2}$.

2.1. Material and methods

Chemicals were purchased from commercial sources and were used without further purification. All syntheses were carried out under standard conditions, if not otherwise stated. The linear siloxanes were purchased from *Sigma Aldrich* and purified by distillation prior to the tempering experiments.

The NMR spectra were recorded at ambient temperature on a *Bruker Avance III 500* (^1H : 500.1 MHz, ^{29}Si : 99.4 MHz) with a QNP-cryo probehead. The chemical shifts are reported in δ (ppm) and are related to tetramethylsilane (0.00 ppm) as an internal standard. In order to increase the quality of the ^{29}Si -NMR spectra we added a small amount of chromium(III) acetylacetonate ($3 \cdot 10^{-3}$ mol/L) as shiftless spin relaxation reagent to the deuterated solvent. Furthermore, the inverse gated decoupling was used for recording the ^{29}Si -NMR spectra. The coupling constants are given in Hz and the multiplicities are abbreviated as follows: s=singlet, d=duplet, m=multiplet.

The GC/MS measurements were conducted on a *Varian 3900 GC* unit coupled with a *Varian Saturn 2100 T* mass spectrometer (column: VF-5 ms, $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$, carrier gas: helium, flow rate: 1 mL/min, injector: CP-1177, split 1:50, EI: 70 eV).

For the tempering experiments 150 mg of the siloxane sample were sealed under vacuum (10^{-2} mbar) in prescored 1.5 mL borosilicate glass ampoules (*Wheaton*). The ampoules were tempered in a *Nabertherm CP330* furnace. After the tempering experiments the composition of the siloxanes was analyzed via GC analysis on a *Varian GC 3900* unit (column: VF-200 ms, $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$, carrier gas: helium, flow rate: 1 mL/min, injector: CP-1177, split 1:50, detector: FID 39xL, 250 °C). Due to the similar chemical behavior and carbon content of the analyzed siloxanes the GC-results for these siloxanes are given in relation towards each other. These results are therefore in satisfying accuracy.

The thermal experiments in steel ampoules were conducted at the *Wacker Chemie AG*. The steel ampoules had a volume of 14 mL and were filled with 7 g of the siloxane. The ampoules were filled and closed in a glove-box (MBraun) with Argon as protective gas. The lid was tightened with a wrench. The ampoules were tempered in a *Carbolite LHT* oven. The GC analysis was conducted on an *Agilent 6890 plus* unit (column: HP-5, $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$, carrier gas: helium, flow rate: 1.5 mL/min, injector: CP-1177, split 1:100, detector: A-FID, 320 °C).

Viscosities were measured on a *RheoSense* microVISC viscometer at 23 °C. For each measurement a fresh syringe was used.

The micro-GC measurements were performed on a *Varian 490-GC* (column: cox 1 m, injection volume 1 mL, carrier gas: helium). For the measurements the sealed ampoules were placed in a polypropylene centrifuge tube, which was then sealed with a septum and flushed with argon through a cannula. The gas phase was injected into the GC after the ampoule was broken inside the tube by a soft impact on the tube with a hammer.

2.2. Synthetic procedures

2.2.1. Tris(trimethylsilyloxy)methylsilane, **TM₃**

In a two-necked flask equipped with a reflux condenser, 2.72 g (20 mmol, 1 equiv.) of trimethoxymethylsilane were dissolved in 13.2 g (100 mmol, 5 equiv.) trimethylsilyl acetate. To the mixture 1.59 g

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