

List of changes

We thank both reviewers for the positive assessment of our manuscript. A point-by-point list of changes and responses is given below.

Reviewer #1

This manuscript outlines a study on molecular dynamics simulation of silicone oil polymerization from combined QM/MM modeling. The findings are positive and provide valuable recommendations despite the increasing complexity of the forming bundle of polymer strings, as well as appealing performance for tackling both elastic and viscous relaxation. To enhance the manuscript's persuasiveness, some key areas require improvement before it can be considered for acceptance by the editor.

1. The introduction section lacks sufficient information about previous research.

While still aiming at keeping the introduction concise, we extended the 3rd paragraph to describe the benchmarking of previous modelling approaches in more detail. The new paragraph reads:

While the characterization of a given silicone product is comparably straight-forward to molecular mechanics simulations, modelling of the actual polymerization reactions is more challenging. To go beyond stochastically connecting nearby precursor units, quantum chemical calculations are needed to account for bond formation/dissociation energies [18]. So far, only a small series of combined QM/MM or reactive MM (REAXFF) studies of silicone polymerization was reported [19-23]. To one side, these methods differ in terms of the accuracy in describing the interaction energy of specific configurations. To the other, a potentially even more crucial issue is related to the manifold of structures and network types. Indeed, the simulation methods differ in terms of how relaxation processes are implemented in the course of polymer growth. Proper relaxation gets increasingly important with the overall progress of the polymerization process (and thus the decline of available reaction partners). For this reason, the net turnover (i.e. the degree of curing) may be taken as a benchmark to the modelling protocols [24]. While early simulation studies often reached partial curing leaving 10-30% of precursors unreacted, modern approaches should achieve the curing degree of their experimental/industrial counterparts – which typically gets very close to full conversion of reactants.

2. Multiple citations [15–10]; [11–16]; and [19–23] for a single point should be avoided.

The named citations do not refer to single data points, but to groups of studies which we feel belong together to provide proper accounts of all studies relevant to the discussion in our manuscript.

3. The equation description and the source of this content need to be articulated clearly.

Thanks for the hint, the individual terms of equation 1 are now explained in detail.

4. The authors used with a simulation time step of 1 fs. I strongly suggest to the author that a femtosecond should be thoroughly cross-checked with appropriate references for accuracy.

Thanks for the bringing this up. We indeed used a smaller time step of 0.1 fs for the immediate relaxation after force-field switching. A time step of 1 fs should only be used for the longer-termed sampling. This is now described in line 154.

5. The figures need significant improvement in quality, especially Figure 5.

The quality of the submitted graphic is quite high – maybe there is a conversion issue in your pdf.

Reviewer #2

The paper by Pascal Puhlmann and Dirk Zahn deals with a molecular simulation of the chemical reaction in silico. The authors use two complementary methods of quantum and molecular mechanics (QM/MM) to reproduce the reaction synthesis of the silicone oils trimethylsilanol and dimethylsilanediol mixtures. This article may be of interest to readers involved in the design of QM/MM simulation schemes. However, in its current form there are a number of unclear points in the article, which would be of interest to the authors for clarification. My comments are given below.

1) Line 56. The authors write "trimethyl- and dimethylsilanediol (TMS and DMSD)". The full name of the first compound should be given, as it clearly contains only one OH group, it is probably trimethylsilanol.

Indeed. We corrected this throughout the manuscript.

2) Lines 66-67. The authors write "di/tri-methyl silanediol". As far as I know, all diols contain two OH groups. This is true for dimethylsilanediol. TMS contains only one OH group, so it is not correct to write trimethylsilanediol. It looks like trimethylsilanol. Authors should check the correct spelling of this compound in the text of the article.

Indeed. We corrected this throughout the manuscript.

3) The authors write that they considered the reaction $(CH_3)_3SiOH + HO(CH_3)_3 \rightarrow (CH_3)_3SiOSi(CH_3)_3$ in the gas phase. If two monomers react, there is no strong objection. From the text of the article, I did not quite understand how the authors go into the gas phase and back when the end of the oligomeric chain reacts with the TMS and DMSD monomers, and when the two ends of the oligomeric chains react. This should be clearly stated in the methodological part of the article. That is, the question is: how is the linkage of the reacting comonomer to the oligomer chain taken into account in the gas

phase? This point is lost in the description of the simulation protocol and should be explained. Perhaps Figs 1 and 2 should be updated to make the explanation more clear.

Thanks for this hint. We indeed benchmarked the QM/MM approach by looking into the formation energy of PDMS oligomers, as now described at the end of page 4:

To benchmark the overall polymerization protocol, it is educative to compare our QM/MM results to QM reference calculations. While the dimerization of TMS is used as input parameter in equation 1, we calculated the formation energy in the gas phase of a series of oligomers featuring up to 8 Si-O-Si salt bridges. From this, we found the deviation in formation energy from explicit QM and the QM/MM approximation as only 2 %.

4) When the authors describe the preparation of a mixture in a simulation cell, the size of the simulation cell and the initial density of the comonomer mixture should be specified.

& 5) When describing the gas phase reaction shown schematically in Figure 1, the authors write that they remove water. It is not entirely clear whether the authors are removing water from the simulation cell as new bonds are formed during the reaction? If so, the cell size should decrease as a result of MM modeling because the authors use a barostat. How do the initial and final sizes of the simulation cells compare? Is there enough relaxation time to equalize the density and pressure in the cell? How did the authors control for this? Possible changes in cell edge size should be shown in Figure 4. In this figure, it looks like the cell size is actually decreasing. This is also indicated by the change in density given in the signature.

Indeed. At the beginning of page 6, we now clarified this issue and explicitly stated the underlying volume changes experienced during the curing processes.

Upon polymerization (and removal of the product water) the simulation systems experience considerable volume change. Indeed, the cubic cells of 43.7, 44.0 and 44.3 Å dimensions of the 500:0, 450:50 and 400:100 DMSD:TMS precursors, respectively, reduced to 39.0, 39.5 and 40.0 Å dimensions during the corresponding curing processes, respectively.

6) In the caption to Figure 1, it should be noted that Me is a -CH₃ group.

We changed the figure to explicitly write -CH₃.

7) Figure 2. It is not entirely clear why only TMS dimerization was chosen for the example? Perhaps it is worth discussing how the addition of a new monomer affects the structure of the chain and how the relaxation time of the system changes?

We used TMS dimerization for parameterization of the QM/MM approach. However, the addition of up to 7 further monomers is used for benchmarking, as now described at page 4 (see also point 3). Once identified (and implemented to the force-field) the relaxation time for salt-bridge relaxation is less than 1 ps irrespective of the length of the PDMS chains. It is the search for suitable reaction candidates that provokes extensive MD simulations to allow the polymer network to provide nearby SiOH groups.