Electronic Supplementary Material (ESI) for Soft Matter.

Exploration of the reactive modelling of sol-gel polycondensation in the presence of templates

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Electronic Supplementary Information

Figure S1. a) Evolution of the number of silanol groups, methanol, water and siloxane bridges along three simulations of the polycondensation of MeSA at 800 K. b) Averaged Qn profiles obtained for the same simulations

Figure S2. Profiles of siloxane bond formation during the polycondensation simulations, at 1000 K, of SA, MeSA and SA:MeSA 1:1 mixture.

Figure S3. Percentages of Q^i species *vs* the degree of condensation for the simulations starting with 100% MeSA and SA:MeSA 1:1. *(The discussion of this figure is also included in the document).*

Figure S4. Solvent accessible surface area visualization mode of the same structures shown in Figure 2g, 2h and 2i

Figure S5. Snapshots highlighting rearranged LUT and LUT attached to the siloxane network, obtained from ReaxFF runs at 1000 K.

Figure S6. Side-by-side comparison of the Q^n profiles obtained for the polycondensation simulations at 700 K and 1000 K from a SA:MeSA mixture 1.1.

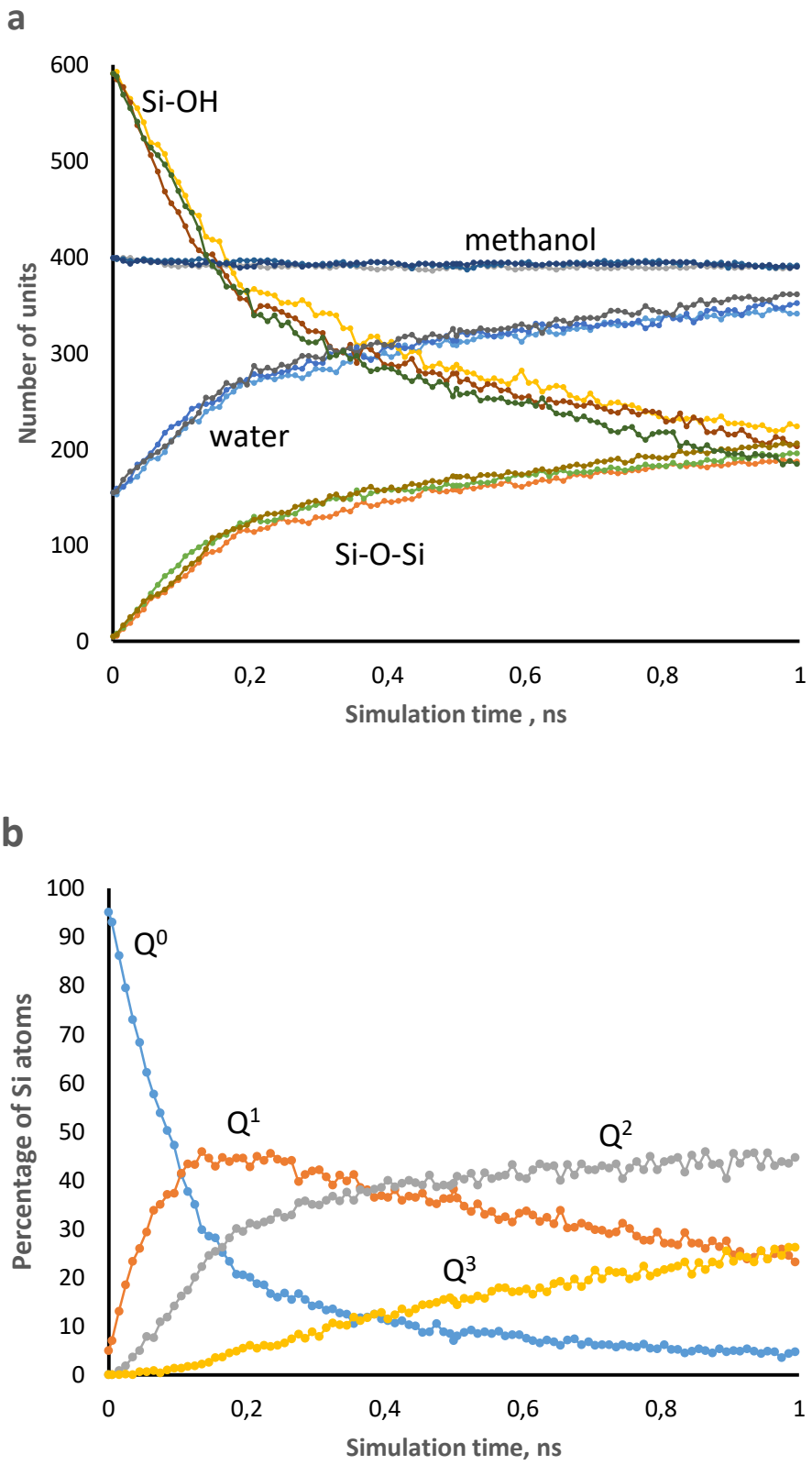

Figure S1. a) Evolution of the number of silanol groups, methanol, water and siloxane bridges along three simulations of the polycondensation of MeSA at 800 K. b) Averaged Qn profiles obtained for the same simulations.

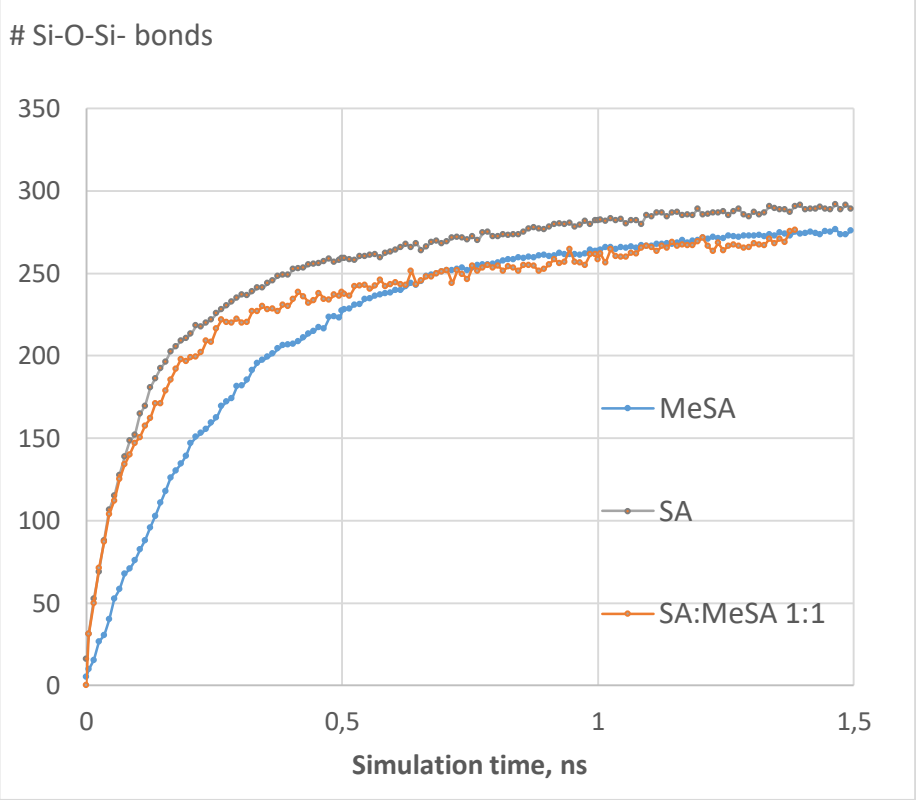

Figure S2. Profiles of siloxane bond formation during the polycondensation simulations, at 1000 K, of SA, MeSA and SA:MeSA 1:1 mixture.

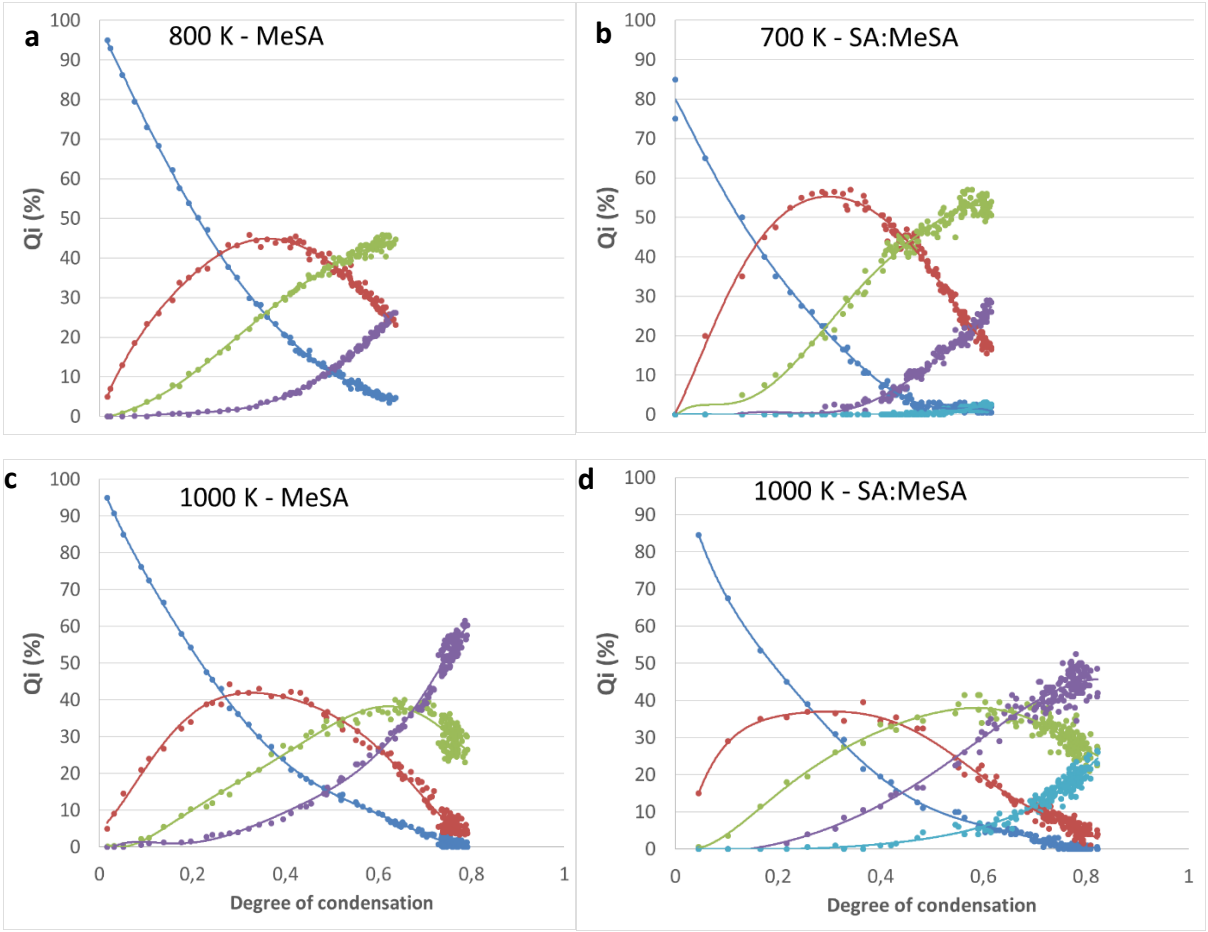

Figure S3. Percentages of Q^i species (Q^0 – marine blue, Q^1 – red, Q^2 – green, Q^3 – purple, Q^4 – cyan blue) *vs* the degree of condensation for the simulations starting with 100% MeSA (a – at 800K, b – at 1000K) and SA:MeSA 1:1 (b – at 700K, d – at 1000 K).

The profiles shown in Figure S2 are identical to those found experimentally [1] except for the peak values of the Q^1 and Q^2 curves. Experimentally, these values were close to 60%, while in our simulations the peaks reached significantly lower values. Simulations run at 1000 K resulted in peak values close to 40%, whereas at lower temperatures the simulations resulted in larger values. Most noticeably, at 700 K a very close agreement with the experimental value was observed (peak values approx.. 55%). Previous simulations run at temperature above 1000K also resulted in low peak values (~40%) [2]. As proposed in [1], the peak values are connected to the relative importance of the possible polymerization paths involved in the process, namely random polymerization and step-by-step assembly of increasingly larger units. Therefore, it appears that simulations run at lower temperatures (700 K and less) are able to replicate more accurately the growing process.

[1] F. Devreux, J. P. Boilot, F. Chaput and A. Lecomte, *Phys Rev A*, 1990, **41**, 6901-6909.

[2] J. D. Deetz and R. Faller, *J Phys Chem B*, 2014, **118**, 10966-10978.

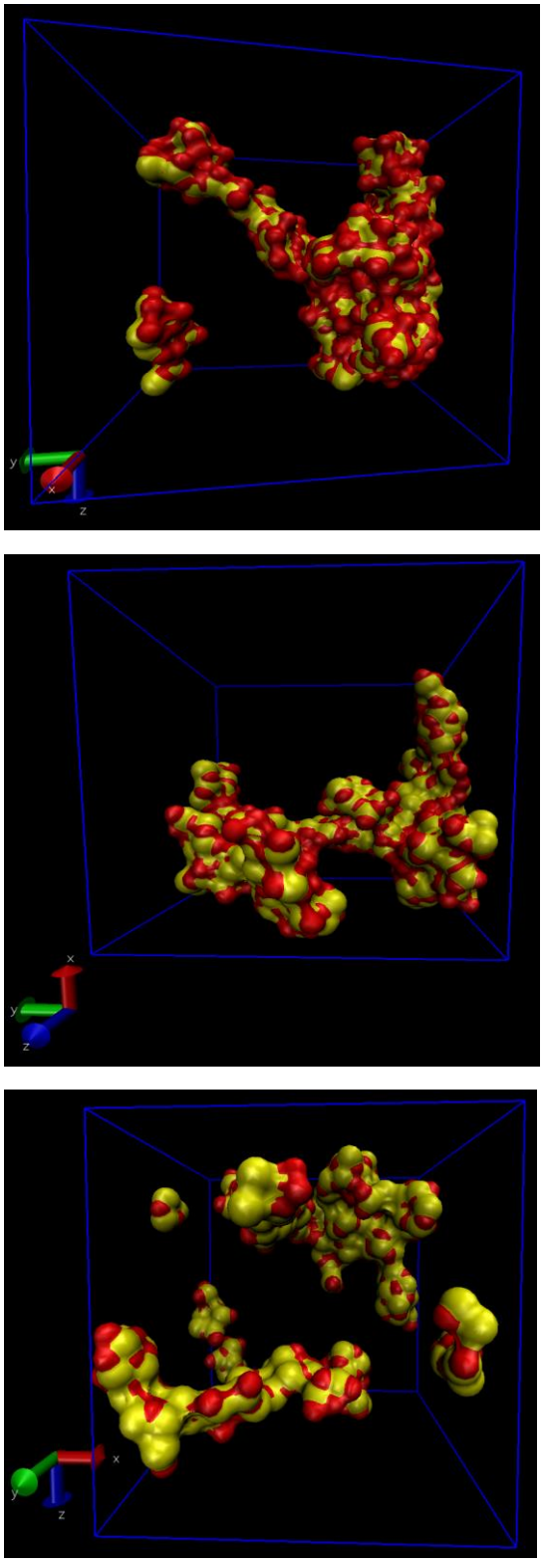

Figure S4. Solvent accessible surface area visualization mode of the same structures shown in Figure 2g (top), 2h (middle) and 2i (bottom).

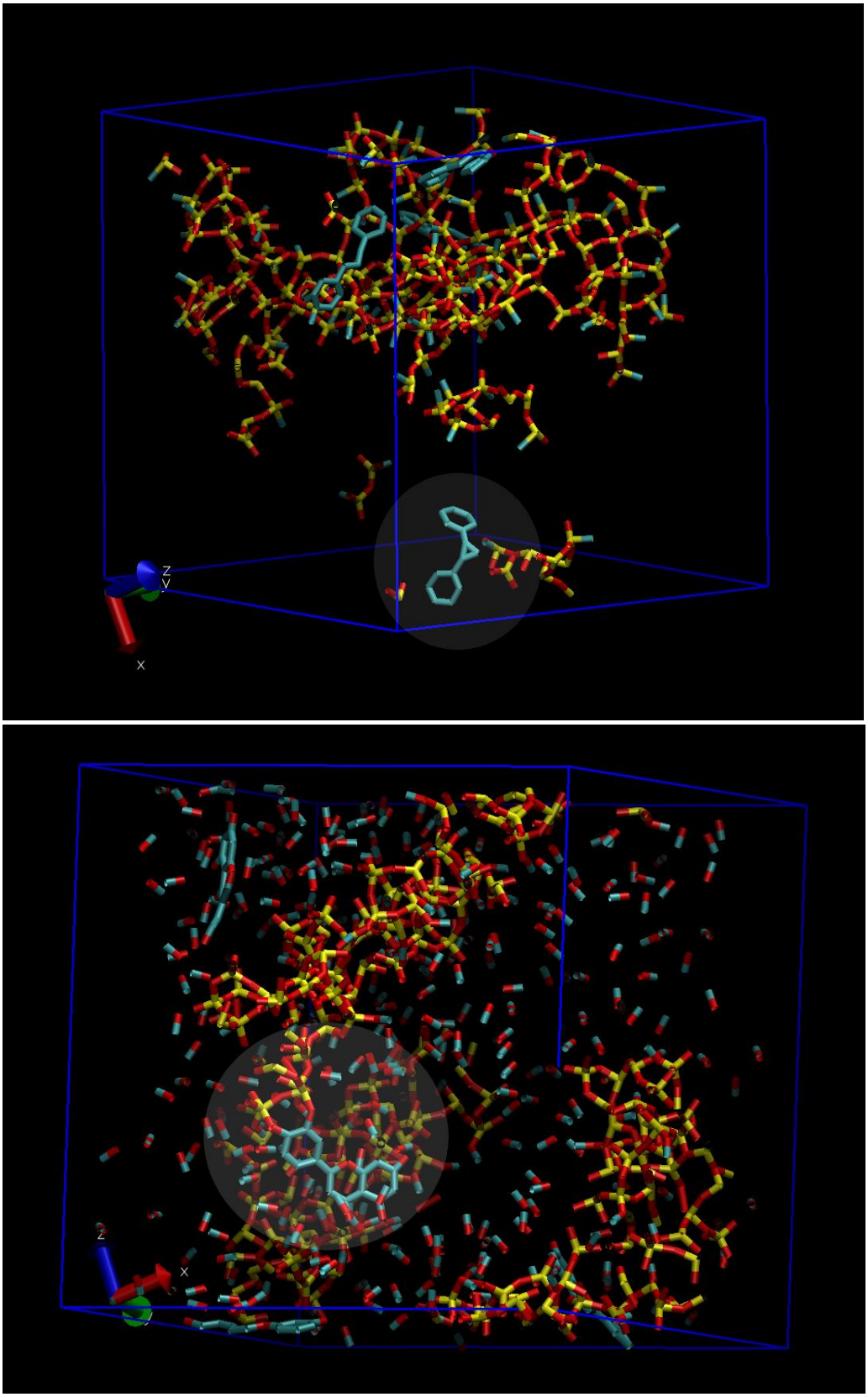

Figure S5. Snapshots highlighting rearranged LUT (top) and LUT attached to the siloxane network (bottom), obtained from ReaxFF runs at 1000 K.

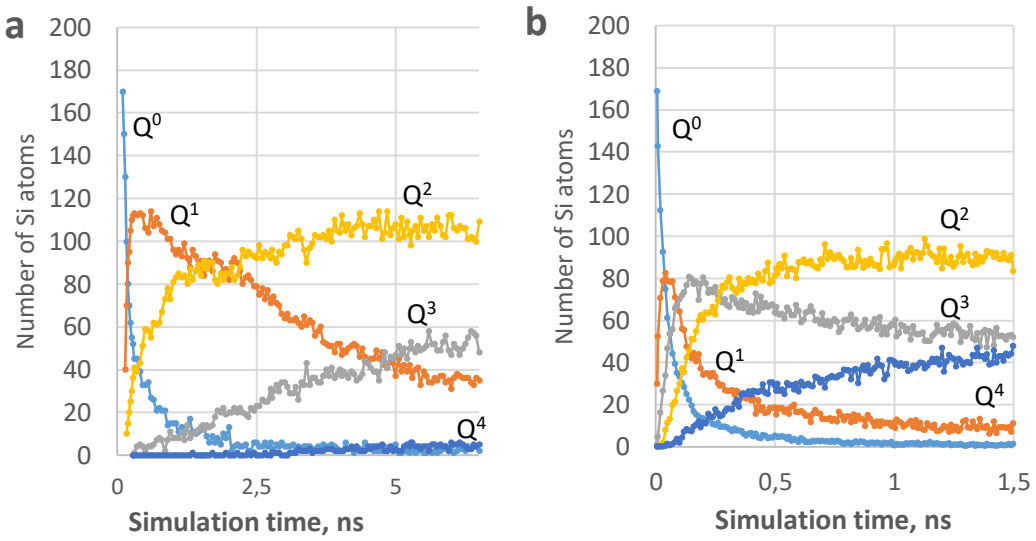

Figure S6. Side-by-side comparison of the Q^n profiles obtained for the polycondensation simulations at 700 K (a) and 1000 K (b) from a SA:MeSA mixture 1.1.