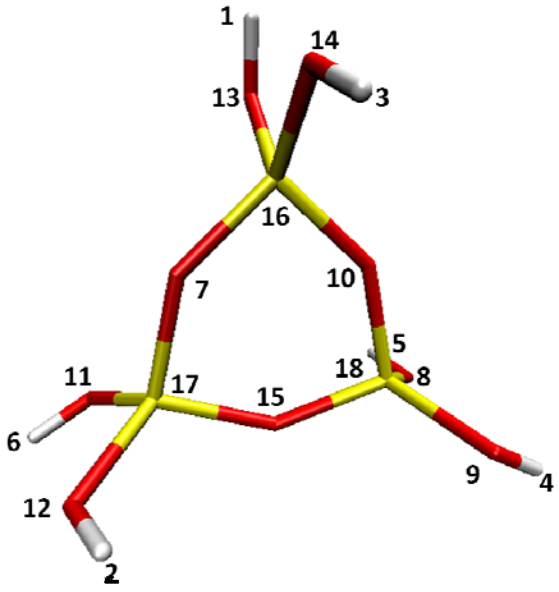
Supporting Information

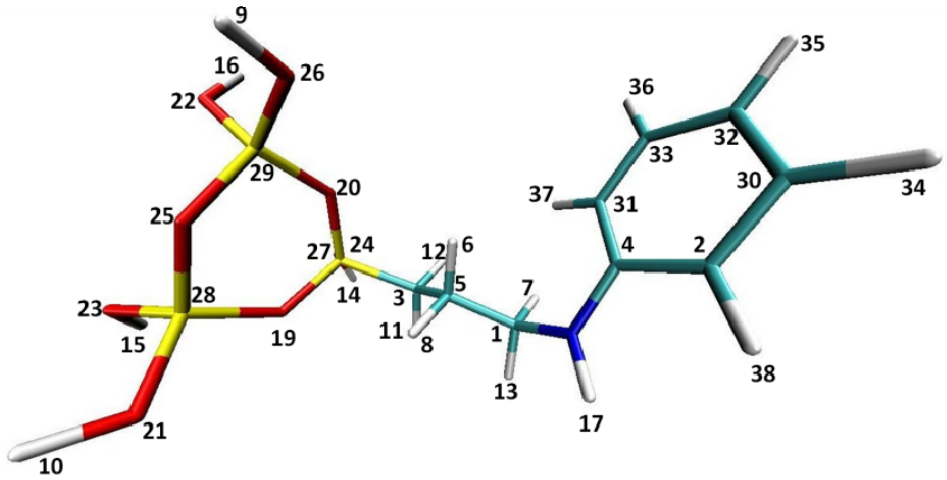
MOLECULAR DYNAMICS SIMULATIONS OF PRE-GELIFICATION MIXTURES FOR THE PRODUCTION OF IMPRINTED XEROGELS

Atom charges for, SI3, SIPA and DAM, computed from a single-point run, using the CHelpG scheme at the MP2/aug-cc-pVTZ(-f) level of theory

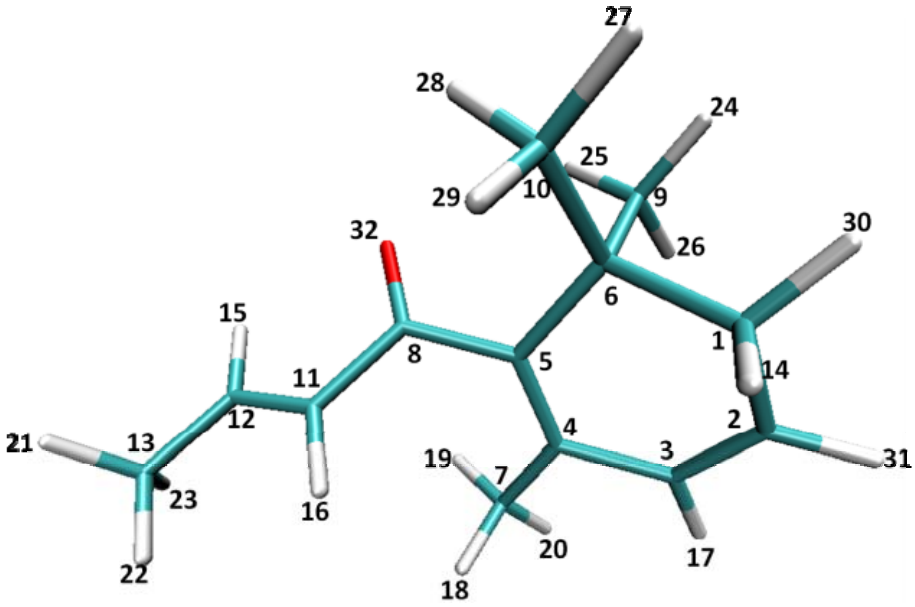
SI3	
atom label	charge (a.u.)
1	0,417333333
2	0,417333333
3	0,417333333
4	0,417333333
5	0,417333333
6	0,417333333
7	-0,643
8	-0,74983333
9	-0,74983333
10	-0,643
11	-0,74983333
12	-0,74983333
13	-0,74983333
14	-0,74983333
15	-0,643
16	1,308333333
17	1,308333333
18	1,308333333



SIPA	
atom label	charge (a.u.)
1	0,209122
2	-0,26671
3	-0,383661
4	0,43343
5	0,0
6	0,0492065
7	0,0
8	0,0492065
9	0,433889
10	0,433889
11	0,079962
12	0,079962
13	0,0
14	0,433889
15	0,433889
16	0,433889
17	0,33583
18	-0,68376
19	-0,825594
20	-0,825594
21	-0,8225684
22	-0,8225684
23	-0,8225684
24	-0,8225684
25	-0,878893
26	-0,8225684
27	1,38715
28	1,6016
29	1,6016
30	-0,08730
31	-0,26671
32	-0,08730
33	-0,08730
34	0,08677
35	0,08677
36	0,08677
37	0,12442
38	0,12442



DAM	
atom label	charge (a.u.)
1	0.225280
2	-0.247306
3	-0.220035
4	0.232048
5	-0.537019
6	0.603736
7	-0.144955
8	0.829418
9	-0.216511
10	-0.343245
11	-0.491737
12	0.095209
13	-0.036954
14	-0.069546
15	0.082919
16	0.155742
17	0.118664
18	0.028588
19	0.043836
20	0.061433
21	0.024953
22	0.036814
23	0.031320
24	0.063915
25	0.005330
26	0.014585
27	0.081400
28	0.044354
29	0.042886
30	-0.046811
31	0.124146
32	-0.592457



Non-standard OPLS-AA parameters utilised.

Non-standard OPLS-AA parameters were taken from ref. 1 unless otherwise stated.

1. Bond lengths were kept rigid at their equilibrium value using the LINCS constraint algorithm.

Bond	length /nm
Si-O	0.161
O(Si)-H	0.094
Si-C (from ref. 2)	0.188

2. Quartic angle potentials were used to calculate angle energy:

Energy (kJ/mol) = $K_2(\theta-\theta_0)^2+ K_3(\theta-\theta_0)^3+ K_4(\theta-\theta_0)^4$

Bends	θ_0 /deg	K_2 /kJ mol^{-1} deg^{-2}	K_3 /kJ mol^{-1} deg^{-3}	K_4 /kJ mol^{-1} deg^{-4}
Si-O-H	118.044	101.496	-114.3387	88.144
O(Si)-Si-C (from ref. 3)	109.82	96.32	-131.4	104.5
C-C-Si (from ref. 3)	112.21	151.5	-85.3	83.8
Si-C-H (from ref. 3)	111.09	120.4	-58.4	0.0
O(Si)-Si-O(H)	111.086	405.2982	-85.2796	330.036
O(Si)-Si-O(Si)	110.926	562.465	-144.118	0.0

O(H)-Si-O(Si) 345.718	116.2621	225.2892	141.795	
Si-O-Si	174.2152	19.517	0.0	0.0
O(Si)-Si-O(Si) 0.0	110.926	562.465	-144.118	

3. Dihedrals were represented by a Ryckaert-Bellemans (R-B) function, of the form:

$$U = \sum_{n=0}^{5} C_n \left(\cos\left(\varphi\right)\right)^n$$

Diedrals	C_0 /kJ mol^{-1}	C_1/kJ mol^{-1}	C_2/kJ mol^{-1}	C_3/kJ mol^{-1}	C_4/kJ mol^{-1}	C_5/kJ mol^{-1}
O-Si-C-H	-0.31380	-0.9414	0.0	1.2552	0.0	0.0 (from ref. 2)
Si-O-Si-O(H)	0.0	4.004	0.317	0.0	0.0	0.0
Si-O-Si-C	-0.11940	-0.35810	0.57865	0.0	0.47748	0.0 (from ref. 3)
O(Si)-Si-O-H	0.0	-16.443	1.28365	0.591	0.0	0.0
Si-O-Si-O(Si)	0.0	4.225	0.0	0.0	0.0	0.0

4. Lennard-Jones parameters for Si (from ref. 4)

σ (nm)	ε (kJ mol^{-1})
0.44350	0.39748

References.

(1) Pereira, J.; Catlow, C.; Price, G. *J. Phys. Chem. A* **2002**, *106*, 130.

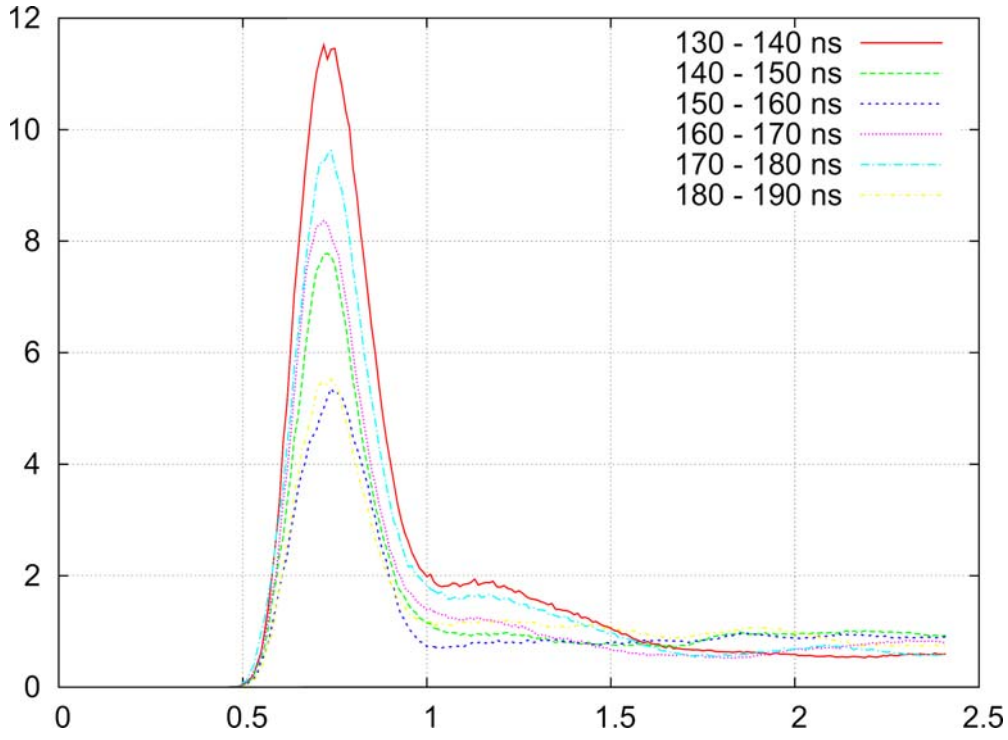
(2) Smith, J.; Borodin, O., Smith, G. *J. Phys. Chem. B* **2004**, *108*, 20340.

(3) Sun H.; Rigby, D. *Spectrochim. Acta* **1997**, *53*, 1301.

(4). Jorge, M.; Gomes, J.R.B.; Cordeiro, M.N.D.S.; Seaton, N.A. *J. Am. Chem. Soc*. **2007**, *129*: 15414.

Evolution of DAM-DAM RDF along the simulation time

(5:1 ratio, SI3 model, Run1)



The absence of a trend in the evolution profile of this RDF shows that the differences between Run1 and Run2 are not attributable to poor convergence. The same behaviour was observed in all studied systems