

Supporting information for

Comment on “Lewis acid-surfactant complex catalysed polymerisation in aqueous dispersed media: cationic or radical polymerisation?” by A. Destephen, L. Lezama and N. Ballard, *Polym. Chem.*, 2020, 11, 5757

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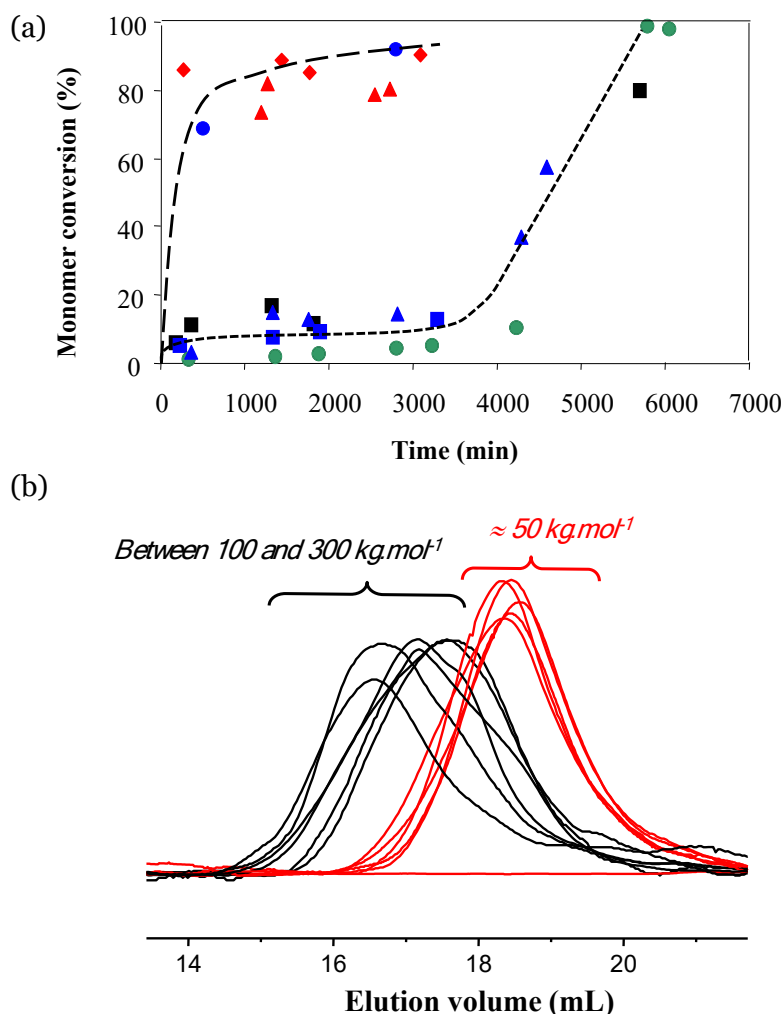


Fig. S1: a) Unpublished results of different runs of pMOS polymerisation with Disponil-based LASC at 60°C (from ref. 11 in the main text). Different catalyst contents were used here. Conditions of polymerisation: pMOS = 1.8 g; H₂O = 3 g; 60°C; Surfactant/pMOS = 22wt%. Content of YbOTf₃ (in mol% compared to pMOS) in different runs : \bullet , 1.3%, \circ , 7%, \blacktriangle , 2.5%, \triangle , 7.5%, \circ , 10%. Radical polymerization (long dash line — —) is fast and not complete, whereas cationic polymerization (short dash line - - -) proceeds first by the generation of low content of oligomers and after a consequent inhibition time, polymer formation. One sees random polymerization process in absence of PCP, e.g. here in the case of 2.5% catalyst (compare blue circles to the other two blue symbols). Lines are only guides for the eye; b) SEC traces of experiments done in same conditions than above with 10 mol% YbOTf₃. One sees two types of distribution, the black one assigned to radical polymerisation and the red one, more monodisperse, assigned to cationic polymerisation.

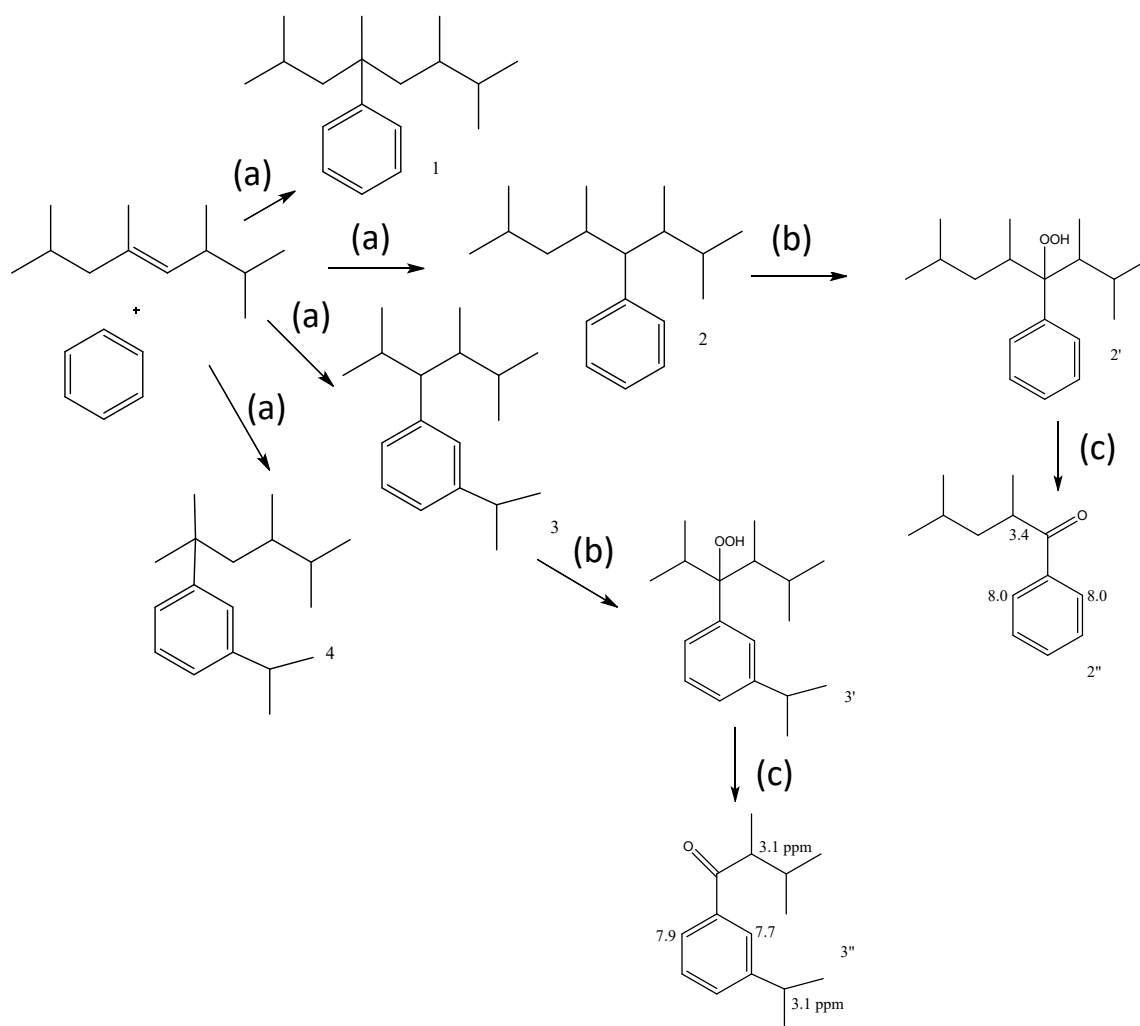


Fig. S2. (a) First step of the synthesis of DBSNa, where different isomers of branched alkylbenzene intermediates are generated before further sulfonation; (b) proposed oxidation of R-CH-Ph bond of alkylbenzene isomers **2** and **3** by O_2 to o-hydroperoxides at α -position to the aromatic ring; (c) further transformation to ketones by decomposition of the primarily formed hydroperoxides. Indicated are calculated chemical shift for **2''** and **3''** using ChemDraw.

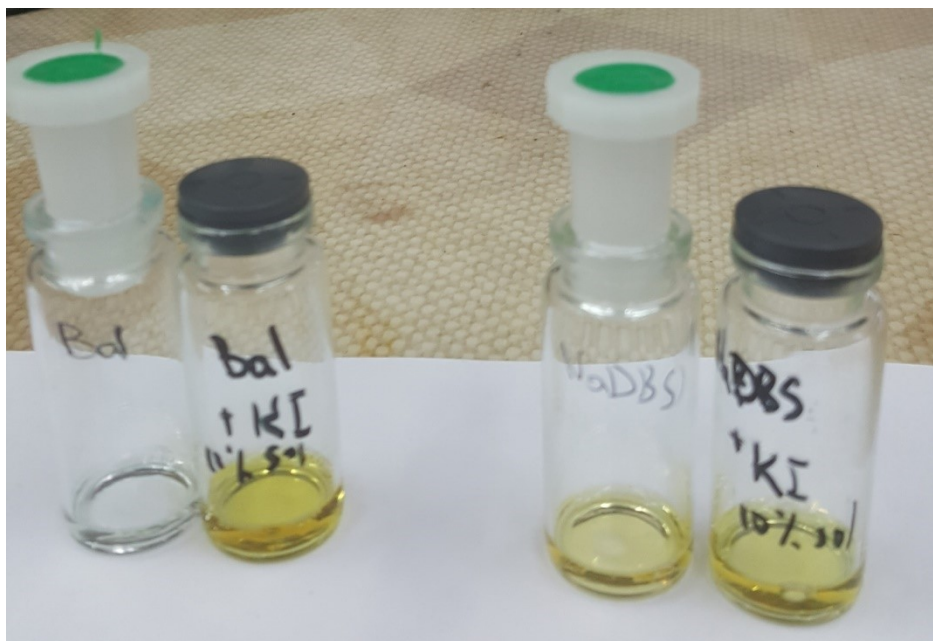


Fig. S3. Qualitative reaction for peroxides. Solutions of Ballard surfactant (left) and our surfactant (right) mixed with 10 % solution of KI. Green lids: original solution, black lids: after KI reaction.

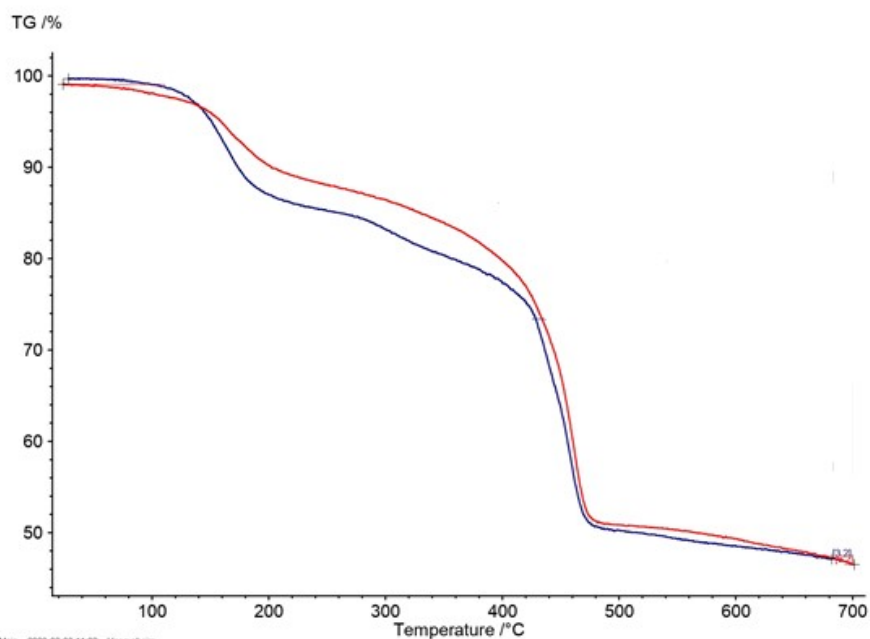


Fig S4. TGA measurements of our DBSNa (in red) and Ballard's DBSNa (in blue). Note that the TGA residue of about 46.5 % and 47.1% for our DBSNa and DBSNa (Ballard), respectively seen here is expected from the decomposition of DBSNa into infusible Na_2SO_4 .

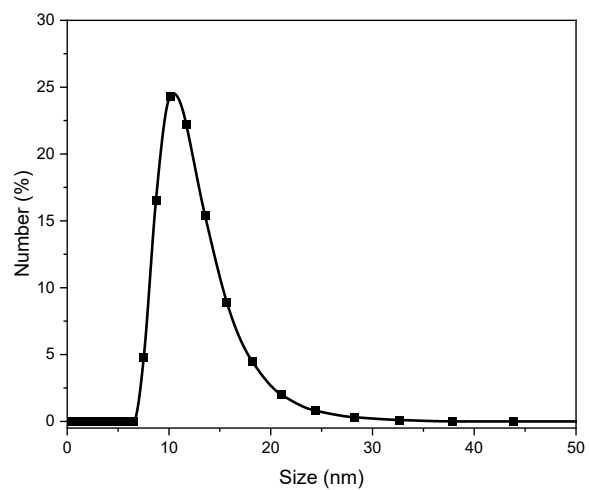


Fig. S5. Typical DLS size distribution of water-soluble micellized LASC prepared from DBSNa ($d_z = 11.9$ nm).