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Irina V Vasilenko, François Ganachaud, Sergei V Kostjuk. 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. *Polymer Chemistry*, 2024, 15 (3), pp.202-206. 10.1039/D3PY00661A . hal-04774288

HAL Id: hal-04774288

<https://hal.science/hal-04774288v1>

Submitted on 8 Nov 2024

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COMMENT

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Introduction

In a paper published in 2020 in *Polymer Chemistry*,¹ Destephen et al. have investigated the polymerisation of various monomers in aqueous dispersion catalysed by so-called Lewis acid-surfactant complexes. These complexes were described extensively in prior publications by us and others as efficient catalysts for cationic polymerisation in aqueous dispersed media (*vide infra*). Polymerising different monomeric systems, they questioned the mechanism of polymerisation as it has been proposed previously, on the basis of extensive and multiple striking experiments. They proved without a doubt that radical production from their surfactant mostly drives the polymerisations. Still, it does not erase conclusions published before by us and others about cationic catalysis; indeed, as we show below, their primary reactants, and the choice of reaction conditions, are not favouring cationic polymerisation. We propose in the following new experiments and interpretations to prove this assertion, thanks to Dr Ballard's help who sent us some of his surfactant. We finally propose a more elaborated mechanism based on our most recent observations, unpublished so far, to potentially explain the synthesis of (far too) large molar masses in this system.

Brief state of the art on LASC polymerisation

LASC discovery was first applied to organic chemistry reaction, where it was shown that interfacial reaction of lipophilic reactants was enhanced by the presence of this hybrid surfactant/catalyst complex.^{2,3} Several studies showed that for an efficient catalysis, the LASCs had to be at least micellisable in water,⁴ which is not the case e.g. with sodium dodecyl sulphate (SDS).⁵

In the last fifteen years or so, we came up with two types of LASCs, one complexed with an electrosteric surfactant with sulphate end-group (so-called Disponil Fes32)⁶ and one with a particular highly-branched dodecyl benzene sulfonate sodium (*hb*-DBSNa).⁷ The first LASC would only polymerise *p*-methoxystyrene (*p*MOS) at 60°C in very specific conditions, whereas the second one could also polymerise styrene (Sty), isoprene (IP), β -myrcene even at moderate temperatures (typically 40°C). In both studies, we systematically looked for the conditions where competitive radical polymerisation could be avoided, and found out that the addition of a weak, organic Bronsted acid (namely pentachlorophenol or PCP) both favoured cationic polymerisation through protonic initiation and inhibited radical polymerisation. The same *hb*-DBSA surfactant/ytterbium complex was then used by some French colleagues to graft polyisoprene on graphene oxide sheets dispersed in water by cationic polymerisation *in situ*.⁸ Note that other types of surfactants tested in this study failed to promote the grafting reaction. In a following, more detailed study,⁹ we then described the influence of each reactant (metal, ligand, initiator) on the mechanism of polymerisation and confirmed, once again, that cationic catalysis is responsible for the polymerisation.

One key point in all these experiments is the necessity to process the reaction in *emulsion*. We confirmed by different means the generation of submicronic droplets, which size varies with conversion from 0.5 to about 0.95 μm . This differs clearly from other processes that we have studied (e.g. $\text{B}(\text{C}_6\text{F}_5)_3$) in which polymerisation in suspension (without surfactant) or in dispersion (mixed water/solvent medium) of different styrene derivatives was favored.¹⁰ We have tentatively assigned this phenomenon to the necessity for the LASC complex to penetrate in the core of the droplets and to catalyse very fast propagation and termination reactions, the latter through a retarded transfer to water in this 'dry' environment.

Another clear difference between the two mechanisms of polymerisation lies in the kinetics of reaction and final structure of the polymers: (thermal) radical polymerisation proceeds at random kinetic rates and leads to high yield of polymer chains of large molar masses (M_n around 100 kg/mol); whereas,

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cationic polymerisation generally starts after an inhibition period, proceeds very sluggishly to generate oligomers and then finally leads to polymer chains of lower molar masses (M_n of about 50 kg/mol). Figure S1 reports unpublished kinetics and SEC results from the Ph. D. work of Dr. Séverine Cauvin¹¹ that show the difference of reactivity and final molar masses between the two assigned mechanisms.

Initial remarks on Ballard et al.'s study

The work proposed by Destephen et al¹ covers a large range of experimentation but does not finally cover a large range of conditions and especially those favouring cationic polymerisation. Note that there are some inconsistencies in their results that we do not wish to discuss here, since it is not at the heart of our comment.[‡]

First of all, several monomers were tested: styrene, *p*MOS, β -pinene, methyl methacrylate (MMA) and acrylamide. The first 3 monomers polymerise by conventional cationic polymerisation, whereas the latter 2 are radically polymerised. Another relevant monomer, that has a specific discriminating cationic polymerisation behaviour in LASC process, is isoprene, was unfortunately not been considered by the authors (*vide infra*).

Almost all experiments were carried out at 60 °C, which we have shown before to favour the competition with radical polymerisation (see also Figure S1). The only exception is *p*MOS polymerisation at 40 and 0 °C that logically did not allow polymerisation to proceed (albeit with Sc metal, see ref.9). Other polymerisation at R.T. were carried out in absence of surfactant, and using a phosphonic acid as initiator (on the basis of Storey and Scheuer's study)^{12,9}

Another issue is the fact that nowhere in the article is mentioned the state of the dispersion, the size of the droplets or the evolution of the colloidal stability with time and conversion (although the description of DLS is reported in the experimental part). This is strikingly important when reporting on emulsion system, since we know that variations in surfactant

content and metal/surfactant ratio can have a strong impact on the overall polymerisation process.⁹

Comparison of DBSA surfactants

As we have shown before, the nature of the surfactant is central to the success of the polymerisation. Thankfully, Dr Ballard kindly sent us some of the DBSA surfactant they used so that we could compare it with our surfactant before testing its catalytic efficiency in our hands.

In Figure 2, we show different characterisations that were done on DBSNa (Ballard) in comparison with our DBSNa.[‡] Specifically, ¹H NMR spectra of both surfactants are almost identical (Figure 1a). The signals corresponding to oxidised hyperbranched dodecene groups between 3.4 and 4.2 ppm are absent or too small due too low content in analysed sample. The slightly higher relative intensities of signals of aromatic protons in ortho and para positions as compared to the signal at 7.5 ppm indicate that DBSNa (Ballard) is more branched than ours.

Ballard et al proposed that radical sources at the heart of their results could be the presence of very few phenyl and sulphur-based radicals generated by photolysis of the sulfonate groups on the long run. We rather infer that oxidised alkenes, as described elsewhere,¹³ could play this role. The transient peroxide groups thus obtained gradually transform into non-reactive ketones, that show up in the NMR spectrum (see also Figure S2 for the mechanistic pathway of oxidation).

We then checked the presence of peroxides in both surfactants via a colorimetric test.¹⁴ In the presence of peroxides, a potassium iodide (KI) solution turns yellow via a redox reaction leading to the formation of iodine (I₂). Since our DBSNa is by itself slightly coloured, we used UV-Vis spectroscopy to unravel the redox reaction. As shown in Figure 1b, the addition of KI to the aqueous solution of our surfactant does not change the UV-Vis spectrum, indicating the absence of peroxides. In contrast, the addition of KI to DBSNa (Ballard) was visually accompanied by the appearance of a yellow colour in

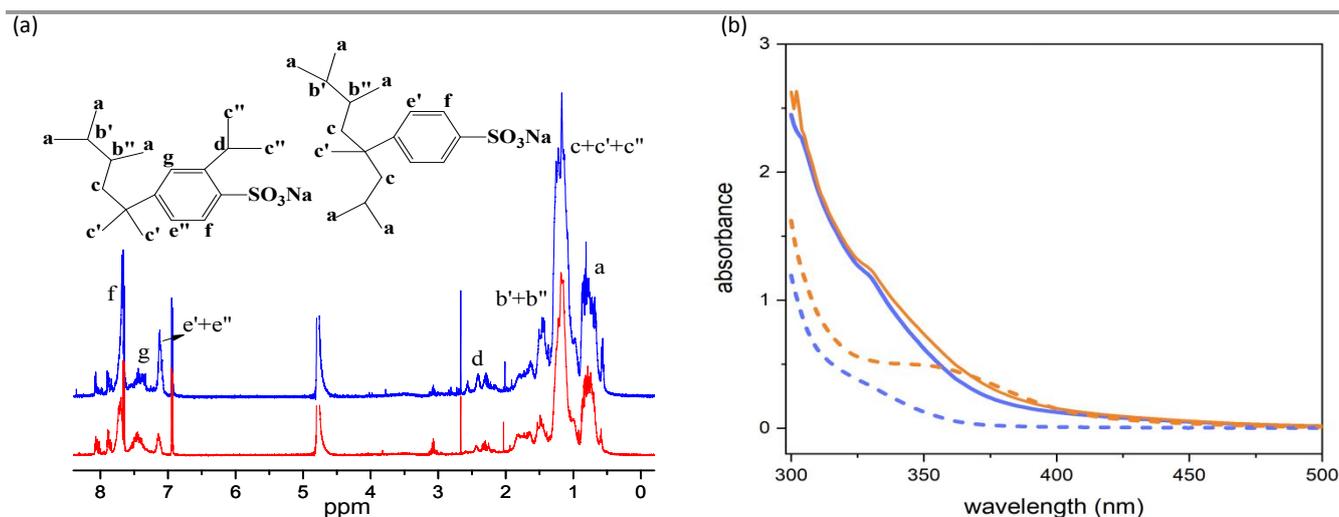


Figure 1: (a) Proton NMR of our DBSNa (in blue) and DBSNa (Ballard) (in red). Please note the slight difference in aromatic peaks ascribed to ortho and para positions (signals f and e+e'). Peaks at 8.05, 7.87 and 3.06 ppm, are tentatively ascribed to ketone environments (see supporting information for full explanation); (b) UV-Vis of solution of DBSNa (plain curves) and DBSNa (Ballard) (dashed curves). Colours are for before (blue) and after (orange) addition of aqueous solution of KI (see also photos of samples in Figure S3).

place of original transparent solution (see Figure S3). Also, a new peak at 354 nm in UV-vis spectrum indicates the generation of I_2 , thus confirming the presence of peroxides/hydroperoxides in this surfactant.

Besides, TGA showed also a faster degradation for DBSNa (Ballard) tentatively assigned to the presence of peroxide (Figure S4). The LASC prepared from DBSNa (Ballard) and ytterbium chloride gives micelles of very similar sizes as our LASC (d_z of 12 nm by DLS, Figure S5).

Homopolymerisations with the two catalytic systems: similarities and differences

In the following, we present LASC-catalysed homopolymerisations of styrene and MMA, in line with Ballard's study, as well as isoprene (see Table 1).^λ

First, a series of polymerisation of styrene were performed at different reaction temperatures (40 and 60 °C) without and with initiator (PCP) in air atmosphere. At 60 °C, polymerisation of styrene proceeds with comparable reaction rates for both LASCs, formed with our DBSNa and DBSNa (Ballard). The molecular weight and PDI of polystyrenes are comparable and in agreement with the commented study¹ (see in supporting Information of ref.[1], Table S2, exs. 1.2 and 1.3). The poor reproducibility of results of styrene polymerisation was explained by the authors by the influence of O_2 in air on polymerisation reaction. However, we infer that they used wet DBSNa that in turn can lead to deviation from optimal ratio between $YbCl_3$ and DBSNa, thus inducing strong variations on reaction rate and induction period, while still remaining a cationic process.⁹

At 40 °C, the LASC formed with DBSNa (Ballard) is more active in polymerisation of styrene compared with LASC formed with our DBSNa. Polystyrenes synthesised at 40 °C with both LASCs are characterised by similar molecular weights. However, in the case of polystyrene obtained with LASC-DBSNa, one sees that a small fraction of oligomers ($M_n \sim 2500 \text{ g mol}^{-1}$) is also formed. This phenomenon was previously observed for myrcene polymerisation¹⁵ but not for p MOS, isoprene and styrene.⁷ Probably low molecular weight fraction was lost earlier under re-precipitation of the latter corresponding polymers. Opposite activity of LASCs formed with DBSNa and DBSNa (Ballard) is observed when introducing C_6Cl_5OH (PCP) as an initiator. The former complex is more active than the latter one, the yields of polystyrene equal 71 and 46 %, respectively. It should be noted that a strong decrease of the number-average molecular weight from 120 to 20 kg/mol is observed for both LASCs, typical of the previously published cationic polymerisation mechanism.

Homopolymerisation of methyl methacrylate (MMA) was then investigated in the presence of both LASCs at different temperatures. PMMA only formed in the presence of the LASC formed with DBSNa (Ballard) at 60 °C, and not at 40 °C (Table 1). No polymers were obtained in the presence of the LASC formed with DBSNa, neither at 60 nor 40 °C. This fact confirms that the surfactant DBSNa (Ballard) is contaminated with impurities able to generate radicals under heating, whereas ours is not. In presence of PCP as initiator, that is also as radical inhibitor, LASC from DBSNa (Ballard) does not polymerise MMA even at 60 °C, as expected.

As mentioned above, isoprene monomer does not homopolymerise via radical polymerisation in emulsion. We

Table 1. LASC-catalysed homopolymerisations of styrene, MMA and isoprene using the two types of DBSNa surfactants.^a

Run #	Surfactant	Monomer	Temp °C	Time h	Initiator	Conversion % ^b	$M_{n,GPC}$ kg/mol	PDI
1	DBSNa	Sty	60	4	-	75	63	3.1
2	DBSNa (Ballard)	Sty	60	4	-	82	63	2.8
3	DBSNa	Sty	40	6	-	44	117/2.5	3.2/1.3
4	DBSNa (Ballard)	Sty	40	6	-	78	120	3.3
5 ^{c,d}	DBSNa	Sty	40	24	PCP	71	20.6 ^e	1.9 ^e
6 ^d	DBSNa (Ballard)	Sty	40	24.5	PCP	46	17.9	2.7
7	DBSNa	MMA	60	24	-	0		
8	DBSNa (Ballard)	MMA	60	24	-	69	47.4	2.6
9	DBSNa (Ballard)	MMA	60	24	-	71	38.1	4.5
10	DBSNa (Ballard)	MMA	60	24	PCP	0		
11	DBSNa	MMA	40	24	-	0		
12	DBSNa (Ballard)	MMA	40	24	-	0		
13 ^f	DBSNa	IP	40	13	-	89	97.0	3.8
14	DBSNa (Ballard)	IP	40	13	-	91	31.4	3.8
15 ^f	DBSNa	IP	40	24	PCP	92	60.8	2.7
16	DBSNa (Ballard)	IP	40	24	PCP	84	23.1	4.7

^a Polymerisation conditions: $m(YbCl_3 \cdot 6H_2O) = 21 \text{ mg}$; $m(\text{surfactant}) = 78 \text{ mg}$; $V(H_2O) = 0.35 \text{ ml}$; $V(\text{monomer}) = 0.15 \text{ ml}$; mixing rate – 800 rpm. ^b Conversion is calculated without salt in final polymers (24 mg). ^c Data of polymerisation published in ref.7 (Table 1, run 9). ^d $m(C_6Cl_5OH) = 13 \text{ mg}$. ^e data for re-precipitated sample. ^f Data of polymerisation published in ref. 7 (Table 1, runs 10 and 11).

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first checked that polymerisation of isoprene in presence of only the surfactant DBSNa (Ballard) did not proceed at 40 °C after 24h (not shown). At 40 °C, polymerisation with both LASCs proceeded accordingly, with final molar masses lower for the LASC-DBSNa (Ballard) (Table 1). With PCP, polymerisation required more time in both cases and led to lower molar masses, as expected from our previous study. All in all, these latter experiments prove that the LASC made with DBSNa (Ballard) is able to proceed to the same cationic polymerisation as the one promoted by our LASC.

In summary, the surfactant used by Ballard et al generates a LASC that can catalyse both cationic and radical polymerisations, depending whether radical inhibition is controlled or not, respectively. Thus, conclusions drawn by the authors in their article are scope-restricted; the generation of radicals hinders potential cationic polymerisation in their published experiments but their surfactant can also catalyse cationic polymerisation in specific conditions as shown here.

About the very relevant point on the too large molar masses obtained in the LASC process

Even if the cationic polymerisation proceeds without a doubt using suitable DBSNa surfactants, it is nevertheless quite surprising that so high molar masses be reached in the LASC-catalysed polymerisation process. Ballard et al have raised this question in the commented study¹ and a following article,¹⁶ by estimating the maximum molar mass attainable according to know propagation and transfer rate constants. Basically, in optimal conditions, molar masses could theoretically not pass 10,000 g/mol, a molar mass that has never been attained by us and others in other catalytic systems. Rather, at best, 3000 g/mol were generated in inverse emulsion with ytterbium triflate catalyst¹⁷ and dispersion polymerisation catalysed by $B(C_6F_5)_3$.¹⁸

From our experience and unsuccessful works that we did not publish, it seems that the mechanism of polymerisation, even if it is undoubtedly initiated by cationic means, may be more complex than involving simply an extremely bulky ionic pair. Indeed, we have noticed that only singular monomers were active in LASC polymerisation (see Figure 2). All of them, namely styrene derivatives and dienes, bear at least two conjugated double bonds that rotate indifferently in cis or trans position. On the other hand, vinyl ethers, that bear only one double bond, and cyclopentadiene, whose double bonds are in constrained cis configuration, did not produce any polymers in presence of LASC (unpublished results). In Figure 2, we also intuit that butadiene could likely be polymerised by LASC; some DBSNa/rhodium complexes were already described to effectively catalyse the polymerisation of BD in emulsion to generate 1,4-trans polybutadiene.¹⁹ To explain these results, a catalytic polymerisation system was brought in, albeit involving a process quite different from those generally known in catalysis in aqueous medium.²⁰

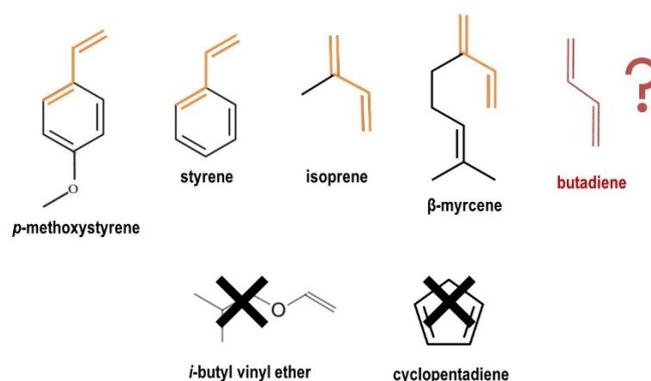


Figure 2: Structures of monomers that were successfully polymerised by LASC (top) and those who failed (bottom). All successful monomers show the same diene structure highlighted in orange. From this interpretation, butadiene has not yet been tested but would logically confirm the series.

We can thus propose that LASC complexes promote a polymerisation that is proton-initiated and involves the coordination of given, specific monomers (freely rotating dienophiles) to the catalyst or the surfactant. We are currently investigating this new proposition of concerted cationic mechanism.

Conclusions

The statement by Destephen et al that LASC-catalysed polymerisation in aqueous dispersion is of radical type and not cationic type is not 100% true; rather, it clearly depends on the conditions in which polymerisation is done and on the starting catalytic materials. In the presence of PCP as an initiator (that is also a radical killer) and by working at moderate temperature, cationic polymerisation is definitively favoured over radical one. Nonetheless, the actual discrepancy between obtained molar masses and those calculated using conventional rate constants for ionic pair-like propagating species, let us believe that the propagating agents are more complex than simple ionic pairs and that research in this field requires more deepening.

Acknowledgements

Dr. F.G. and Pr. S.K thank Dr N. Ballard for providing their surfactant for helpful comparison between their system and ours. Dr. S. Cauvin is acknowledged for the data she gathered to produce Fig. S1.

Author Contributions

I.V.: conceptualisation, methodology, writing original draft; S. K.: funding acquisition, formal analysis, supervision, writing; review & editing; F.G.: writing; review & editing.

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ p.5759 and 5763: the procedure described cannot generate a microemulsion; p.5759 and S.I., exps. 8 and 9 in Table 1 and S3 are inverted and do not show the same conversions; in Figure 5, spectrum of polymer from exp. 5 can a priori not be shown since the conversion reported in Table 1 is nil. S.I., Figure S12: the hard type DBSA does not show peaks at 2-2.5 ppm meaning that the carbon in α position of the phenyl groups does not bear hydrogen, this is not relevant with structures shown in scheme S2.

§ The authors found different results from the original paper but did not comment on that.

λ Experiments on MMA/Sty copolymerisation with our DBSNa will be reported in due course.

f ^1H NMR (500 MHz) spectra were recorded in CDCl_3 at 25 °C on a Bruker AC-500 spectrometer calibrated relative to the residual solvent resonance. Size exclusion chromatography was performed on an Ultimate 3000 device with Agilent PLgel MIXED-C column (7.5×300 mm, particle size 5 μm) and one pre-column (Agilent PLgel 5 μm guard) thermostated at 30 °C, equipped with a differential refractometer. Solutions of the polymers in THF were eluted at flow rate of 1 mL/min. The calculation of molecular weight and polydispersity was based on polystyrene standards (Agilent EasiCal) with $\text{D} \leq 1.05$ and using Chromeleon 7.0 program. UV-vis spectra of DBSNa solutions were recorded with a PerkinElmer Lambda 25 UV VIS Spectrometer.

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Supporting information for

‘Comment on “Lewis acid-surfactant complex catalysed polymerisation in aqueous dispersed media: cationic or radical polymerisation?” by A. Destephen et al, *Polym. Chem*, 2020, 11, 5757’

By Irina V. Vasilenko, François Ganachaud and Sergei V. Kostjuk

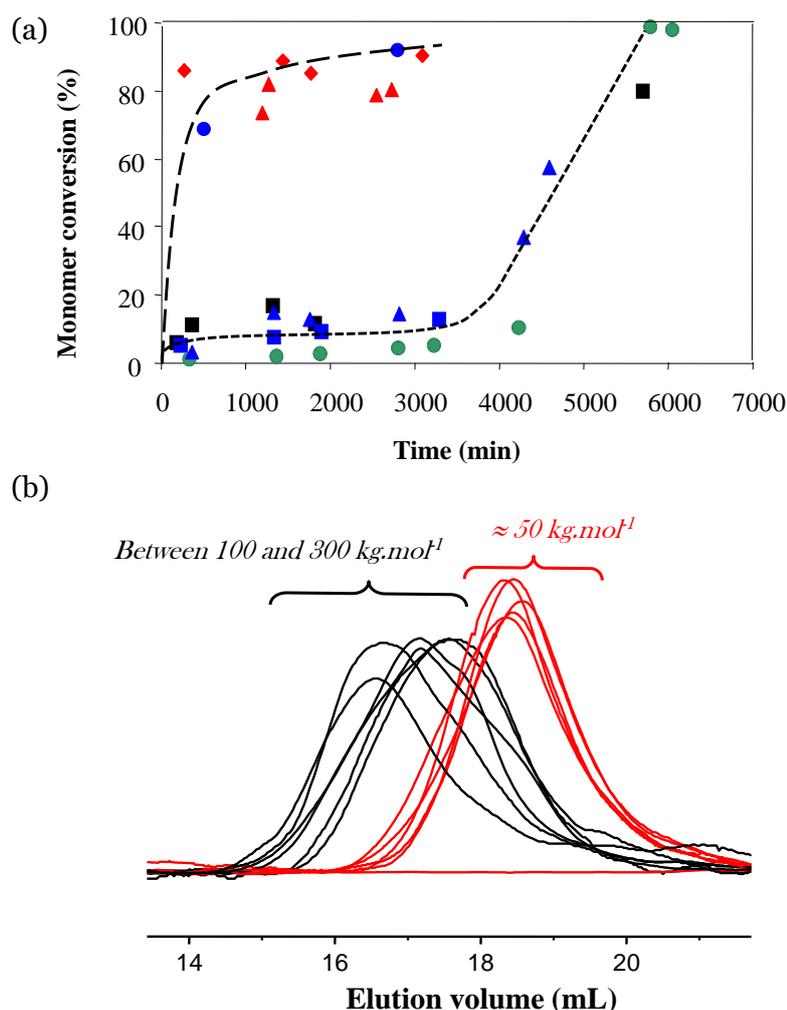


Fig. S1: a) Unpublished results of different runs of pMOS polymerisation with Disponil-based LASC at 60°C (from ref. 11 in the main text). Different catalyst contents were used here. Conditions of polymerisation: pMOS = 1.8 g; H₂O = 3 g; 60°C; Surfactant/pMOS = 22wt%. Content of YbOTf₃ (in mol% compared to pMOS) in different runs : ● 1.3%, ■, ▲, ● 2.5%, ◆, ▲ 5%, ■ 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.

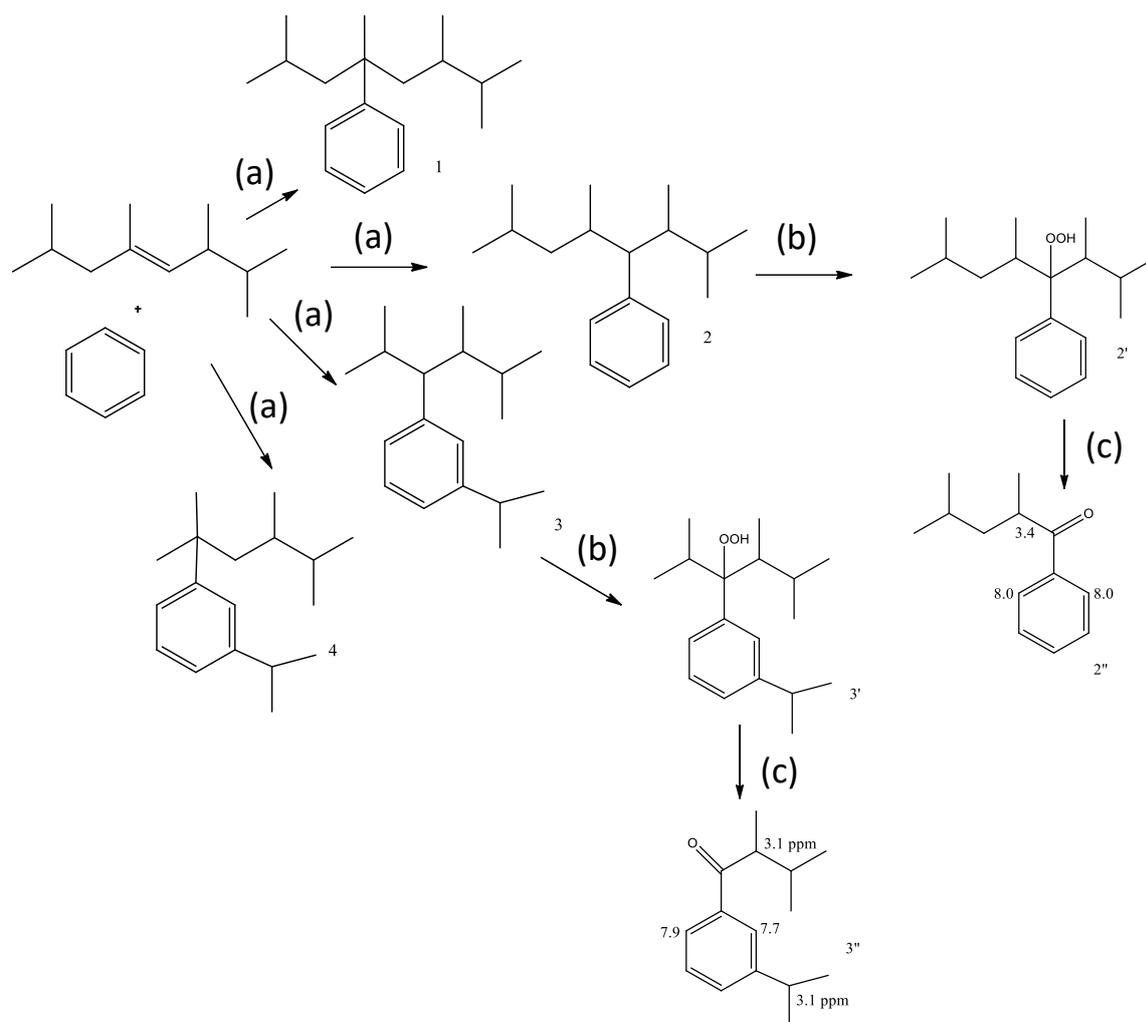


Fig. S2. (a) First step of the synthesis of DBSNa, where different isomers of branched alkylbenzene intermediates are generated before further sulfonation; (b) proposed oxidation of R-CH-Ph bond of alkylbenzene isomers **2** and **3** by O_2 to o-hydroperoxides at α -position to the aromatic ring; (c)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

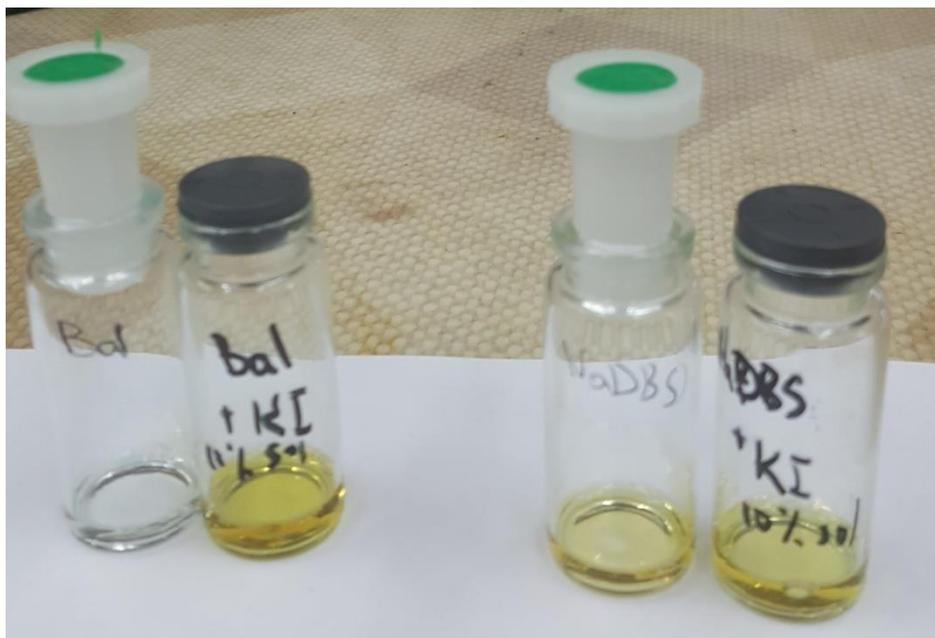


Fig. S3. Qualitative reaction for peroxides. Solutions of Ballard surfactant (left) and our surfactant (right) mixed with 10 % solution of KI. Green lids: original solution, black lids: after KI reaction.

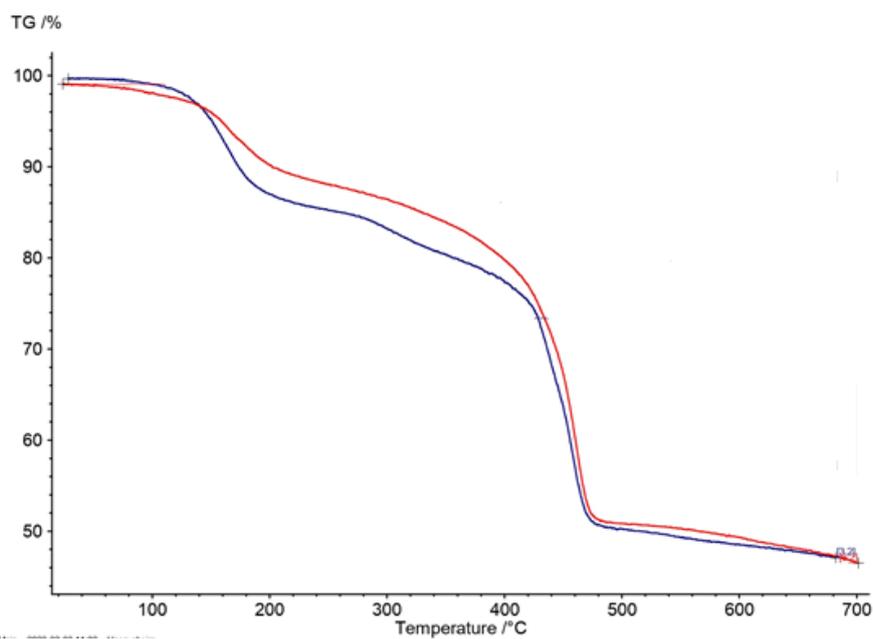


Fig S4. TGA measurements of our DBSNa (in red) and Ballard's DBSNa (in blue). Note that the TGA residue of about 46.5 % and 47.1% for our DBSNa and DBSNa (Ballard), respectively seen here is expected from the decomposition of DBSNa into infusible Na_2SO_4 .

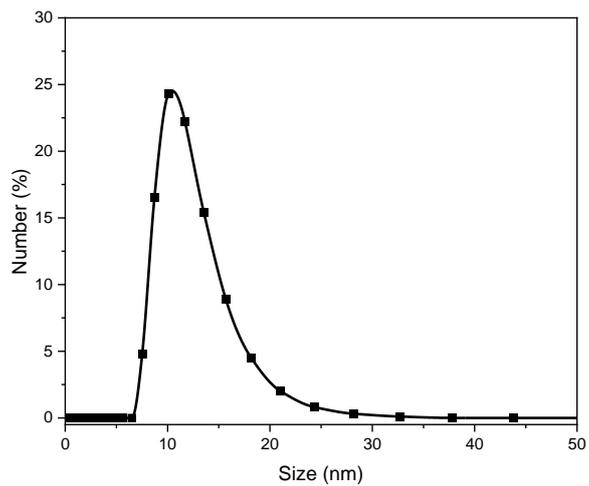


Fig. S5. Typical DLS size distribution of water-soluble micellized LASC prepared from DBSNa ($d_z = 11.9$ nm).