Lewis Acid-Surfactant Complex Catalyzed Polymerization in Aqueous Dispersed Media: Cationic or Radical Polymerization?

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Supporting information

**Structure of sodium dodecyl benzene sulfonates**

Sodium dodecyl benzene sulfonates can be synthesized by a number of routes that lead to slightly different molecular structures and, as shown in this work, can have significant implications for their physical properties. Alkyl benzene sulfonates are typically made industrially by sulfonation of the alkyl benzene with sulfur trioxide (see Scheme S1). This yields the target alkyl benzene sulfonic acid which is then neutralized to give the salt. Due to the commercial importance of these compounds as surfactants, the side products arising from this reaction are reasonably well known and are limited to sodium sulfate, sodium chloride, non-sulfonated alkyl benzenes and trace amounts of metals,[1] none of which would be expected to induce polymerization.

Scheme S1 Sulfonation of phenyldodecane
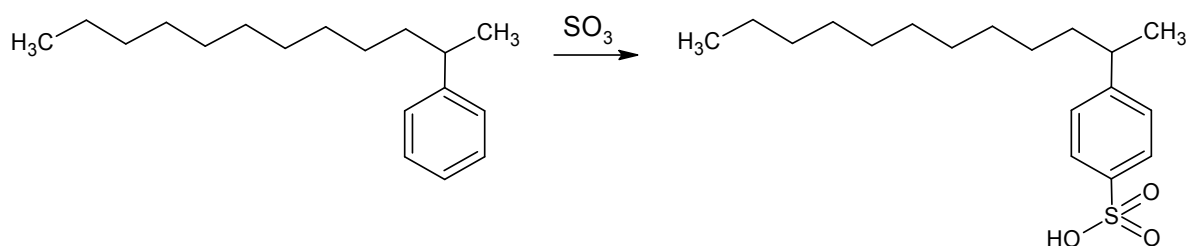
The main difference between the surfactants used in this work is in the alkyl chains. Branched dodecyl benzene sulfonates have historically been produced using tetrapropylene while linear benzene sulfonates use linear olefins (see Scheme S2). Due to the poor biodegradation of tetrapropylene based DBSNa, alternative branched olefins have been developed leading a large range of potential structures for any given commercial DBSNa sample. In addition, regardless of the extent of branching, the starting products can also have a distribution of chain lengths so that the product also has a distribution of alkyl chain lengths. Different isomers (i.e. 2-phenyldodecane, 3-phenyldodecane etc.) are also formed with the relative abundance dependent on the catalyst used in the alkylation.[1]

Scheme S2 Alkylation of benzene using linear olefins to produce linear alkylbenzenes or with branched olefins to give branched alkylbenzenes.
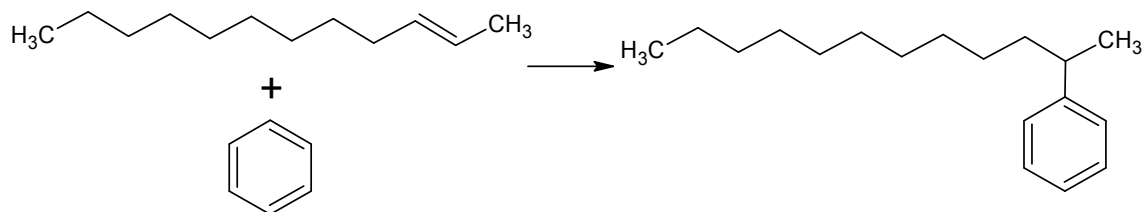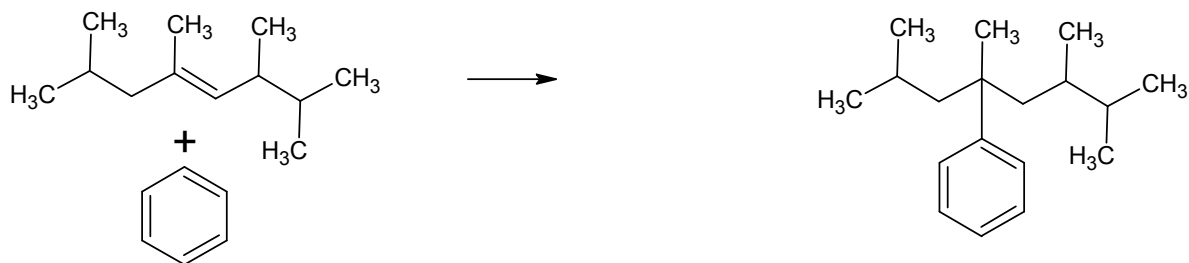
These structural differences can be seen in the NMR spectra of the different sources of DBSNa used in this work as shown in **Figure S1** and **Figure S2**. Although the large number of isomers present in all samples makes precise structural elucidation incredibly challenging, there are several regions in the NMR spectra where clear differences can be observed. In the ^{1}H NMR spectra the two branched forms of DBSNa (hb-DBSNa and DBSNa (hard type)) display multiple peaks in the region around 7 ppm whereas the linear DBSNa only shows two. The peak at ~7.7 ppm can be attributed in all cases to the C-*H* on the aromatic ring that is located closest to the sulfonate group. The other peaks can be attributed to the C-*H* on the aromatic ring that is closer to the alkyl group. As the alkyl group differs between the different samples and have a broad distribution of structural isomers these signals are also substantially shifted going from the linear to branched structures. Although the differences between peaks associated with the alkyl chain of the ^{1}H spectra (1-2.5 ppm) show substantial overlap, more clear differences in the shifts of alkyl groups can be observed in the ^{13}C NMR spectra of the different samples, where in the region 10-50 ppm it can be seen that there is limited overlap between different spectra showing that they are composed of alkyl chains with different structures.

It is important to emphasize that the ^{1}H and ^{13}C NMR spectra of the hb-DBSNa used throughout the work is very similar to that presented by Vasilenko *et al,* to which the present results are compared.
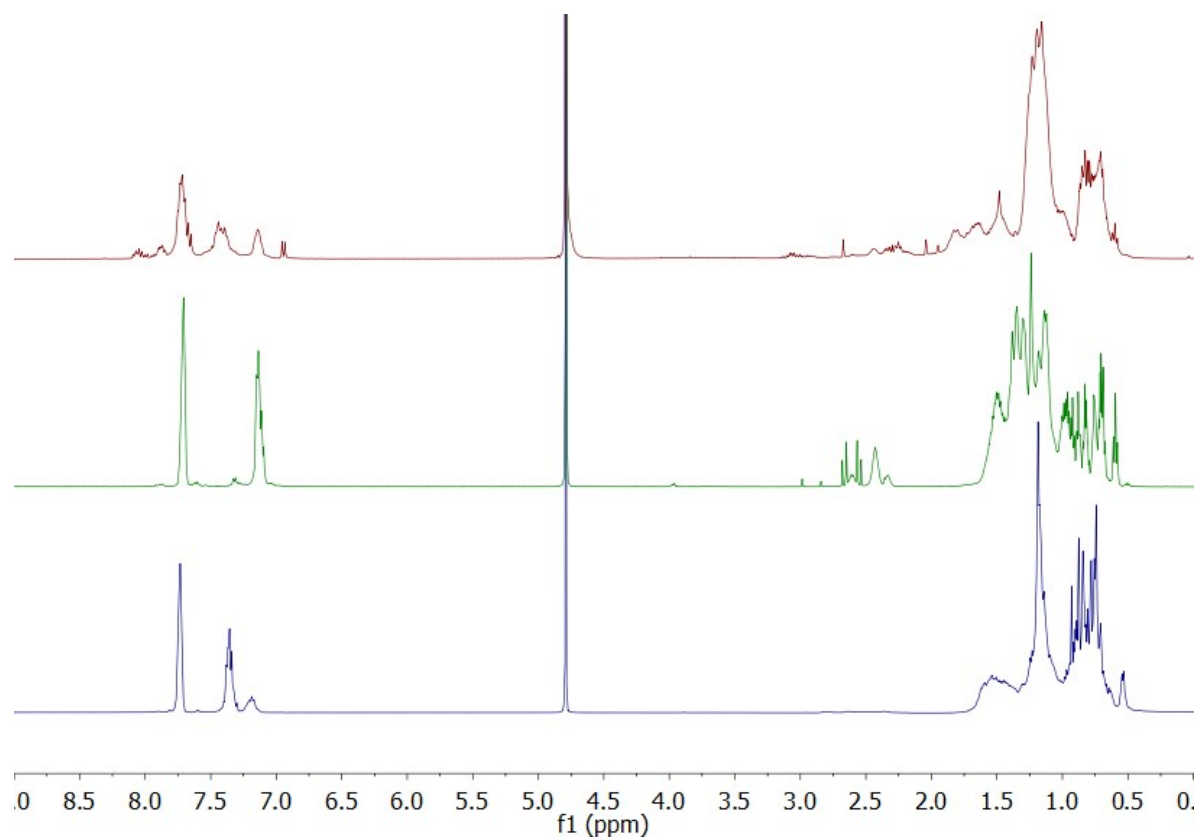
Figure S1 ^{1}H NMR spectra of the three forms of DBSNa used in this work. Top (hb-DBSNa), middle (linear DBSNa), bottom (DBSNa (hard type)).
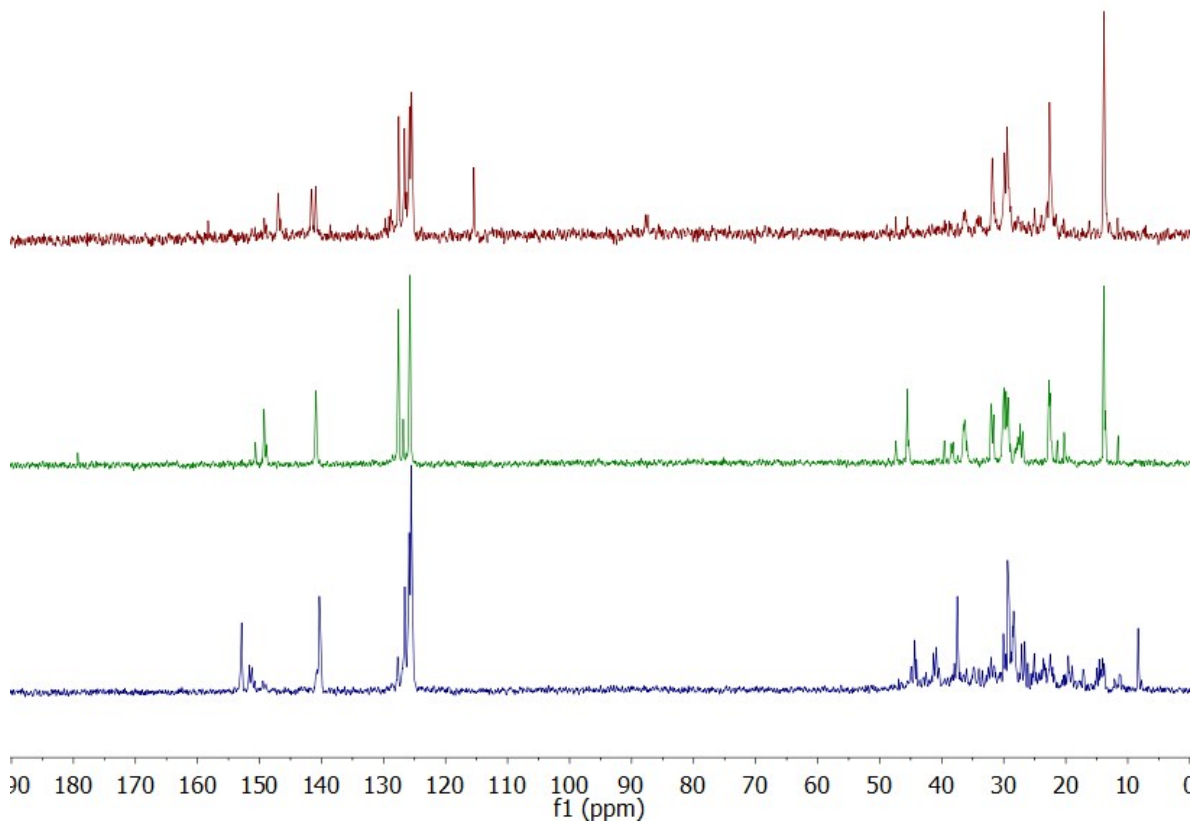
Figure S2 ^{13}C NMR spectra of the three forms of DBSNa used in this work. Top (hb-DBSNa), middle (linear DBSNa), bottom (DBSNa (hard type)).

Table S1 Different sodium dodecylbenzene sulfonate tested.

Surfactant	Provider	Purity	Polymerization
Hyper-branched dodecylbenzene sulfonic acid, sodium salt	Aldrich	Technical grade	Yes
Dodecylbenzenesulfonic acid, sodium salt (hard type) (mixture)	TCI	≥ 95%	No, Precipitate form
Dodecylbenzenesulfonic acid, sodium salt	Aldrich	Technical grade	No, Precipitate forms

Table S2 Summary of the reproducibility experiments.

	Surfactant	Monomer	Time (h)	Conversion (%)	M_n (g/mol)	Đ
Exp 1.1	hb-DBSNa	St	4	91	96,600	2.4
Exp 1.2	hb-DBSNa	St	8	58	65,400	4.0
Exp 1.3	hb-DBSNa	St	8	46	67,300	3.5
Exp 1.4	hb-DBSNa	St	8	89	-	-

Table S3 Summary of the experiments performed to investigate the cationic or radical mechanism implied using ytterbium as catalyst.

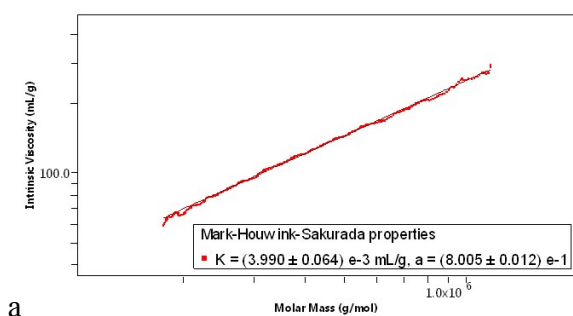|	Surfactant	Monomers	Time (h)	Conversion (%)	M_n (g/mol)	Đ
Exp. 3	hb-DBSNa	pMOS	23.5	41	16,700	1.9
Exp. 4	hb-DBSNa	pMOS	8	91	21,500	3.3
Exp. 7	hb-DBSNa	pMOS + MMA	24	62	28,000	2.5
Exp. 8	-	pMOS	96	71.4	1,300	3.5
Exp. 9	-	pMOS + MMA	96	100	1,800	2.0

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Figure S3 Mark-Houwink-Sakurada plots from SEC/MALS analysis of Exp. 1.2.
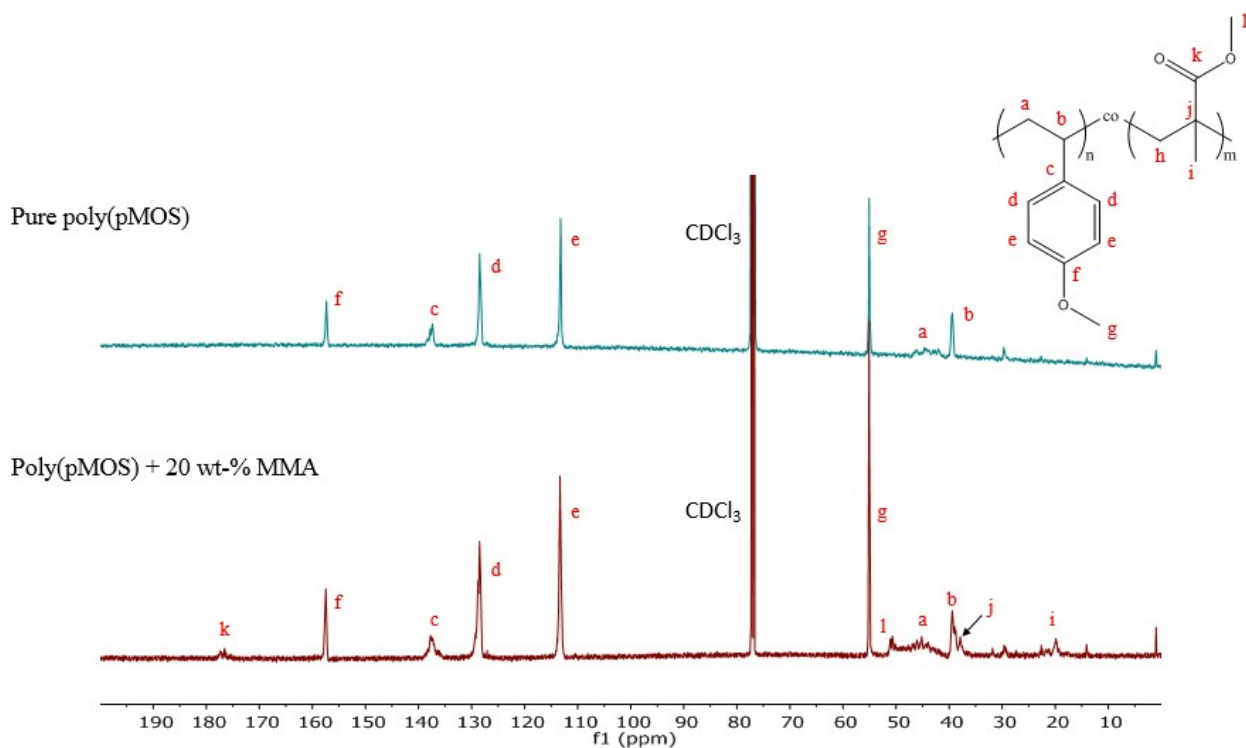
Figure S4 ^{13}C NMR spectra of the polymers obtained in Exp. 3 (top, blue) and Exp. 7 (bottom, red)
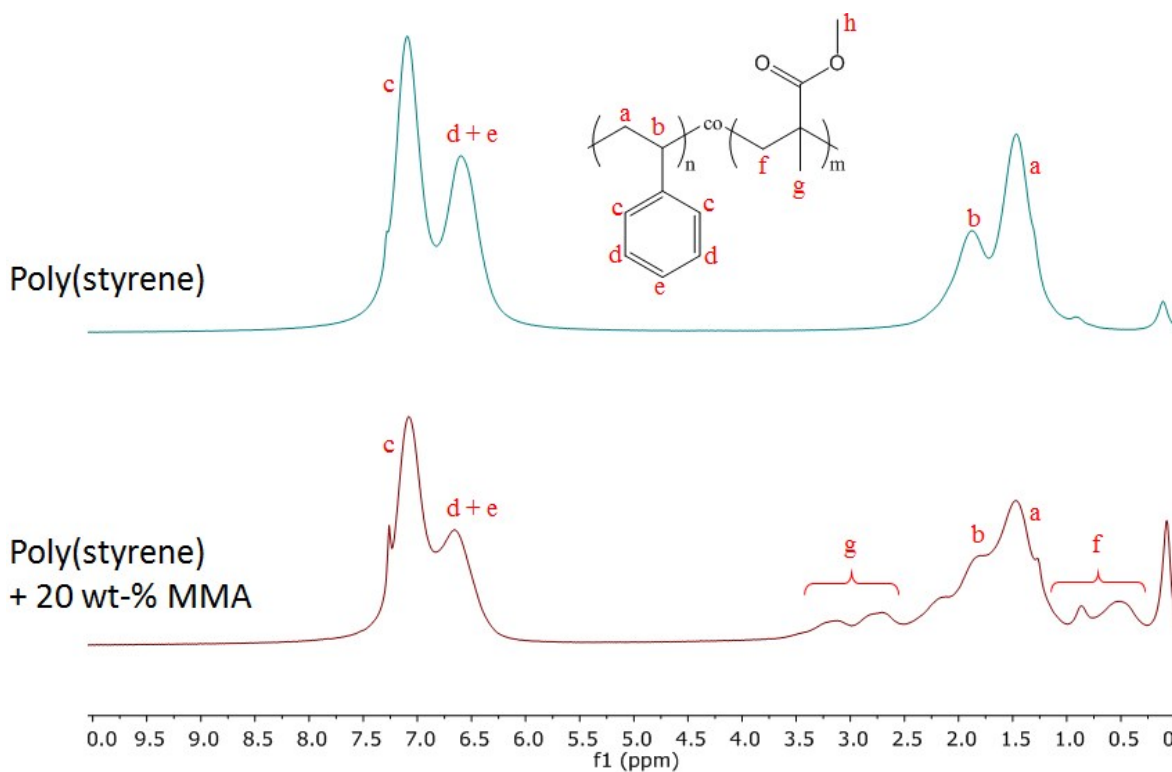

Figure S5 ^{1}H NMR spectra of the polymers obtained using formulation of Exp. 1 but at 40 °C in the absence (top, blue) and presence of 20wt% MMA (bottom, red)
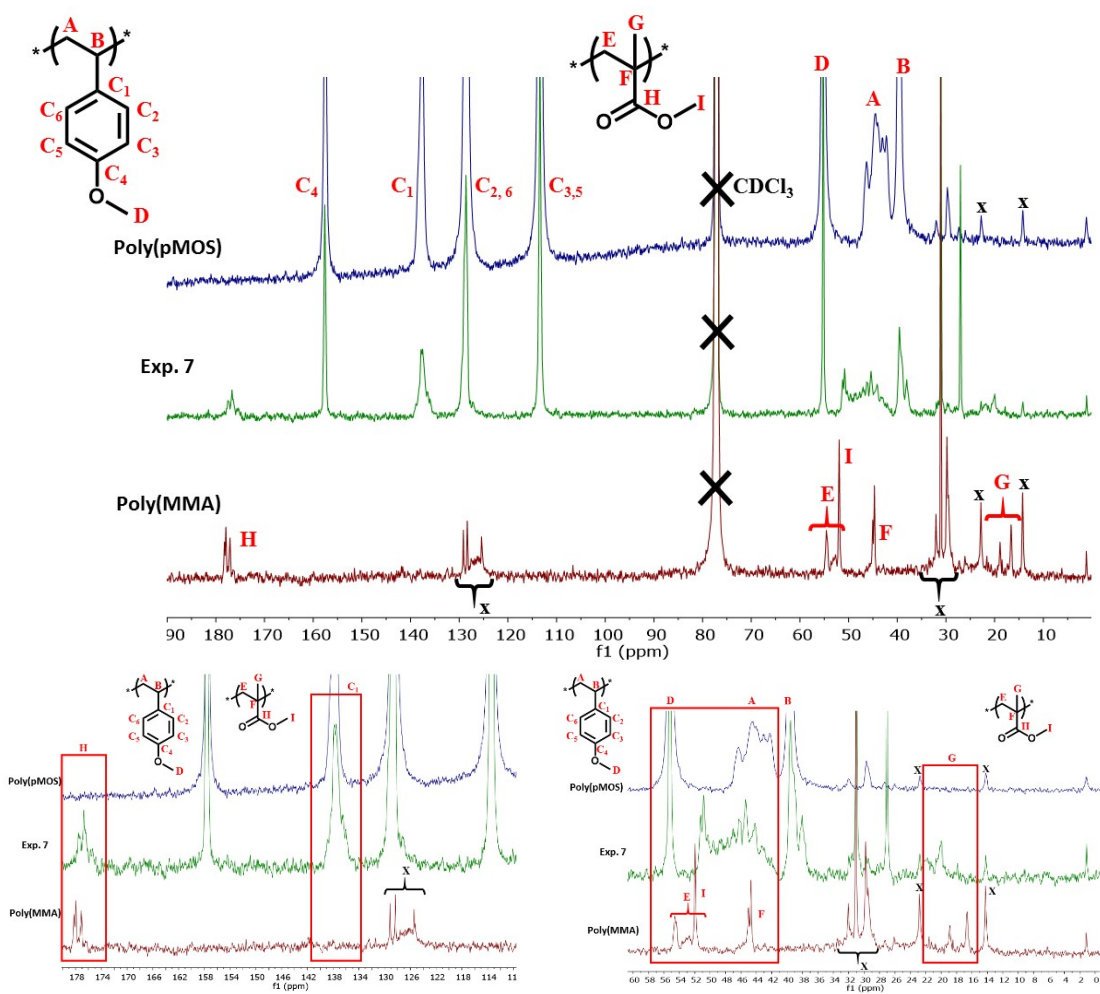
Figure S6 ^{13}C NMR spectra of pure polymer made using pMOS + 20 wt-% MMA (compared to the total amount of monomers) (Exp. 7) as compared to pure poly(pMOS) and pure poly(MMA). The peaks arising from the solvent at 77.2 ppm and from residual DBSNa are marked with an X. The zoomed areas below show that the peak around 20 ppm that is related to the α-methyl group of MMA is shifted substantially and that the peaks in the polymer backbone arising from the pMOS units also show a change in the shape of the peaks indicating formation of a random copolymer.
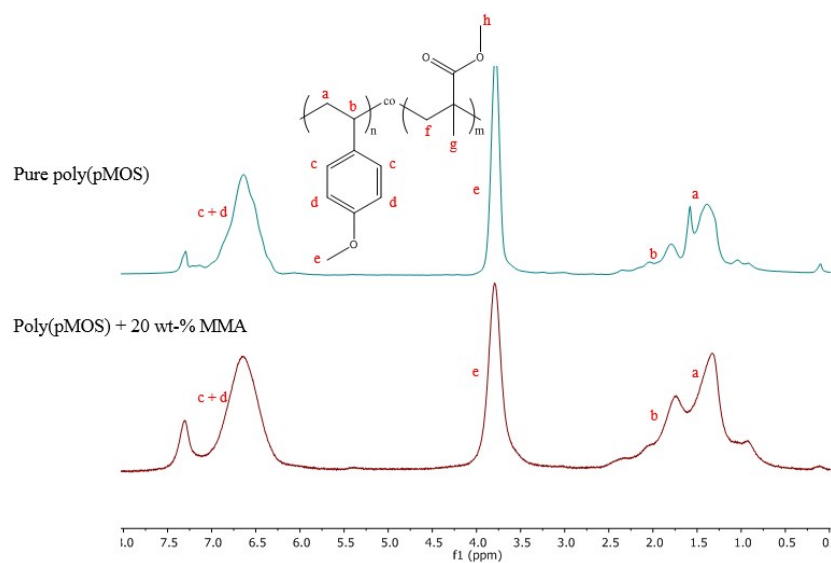
Figure S7 ^{1}H NMR spectra of pure poly(pMOS) polymer (top) and final polymer consisting of pMOS + 20 wt-% MMA (compared to the total amount of monomers) (bottom) for the experiments based on Storey and Scheuer (Exp. 8 and 9, respectively).
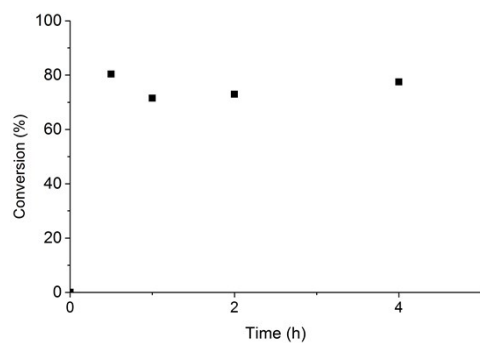

Figure S8 Evolution of the conversion with time for the radical polymerization of styrene in presence of YbCl$_3$.

Figure S9 Highly viscous polyacrylamide solution obtained after 3 min of reaction (Exp 14).
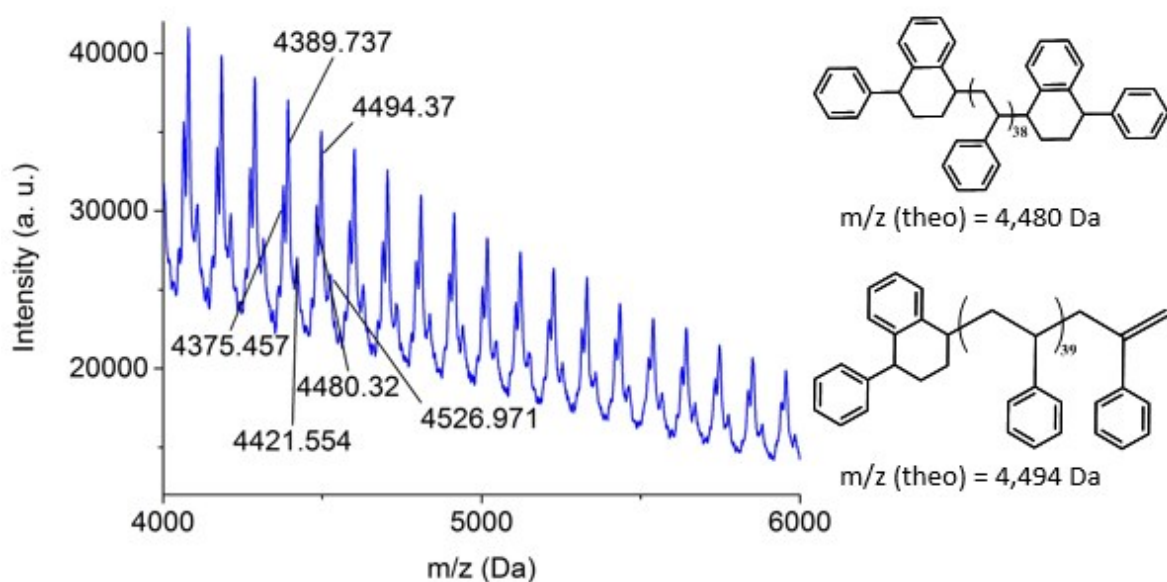

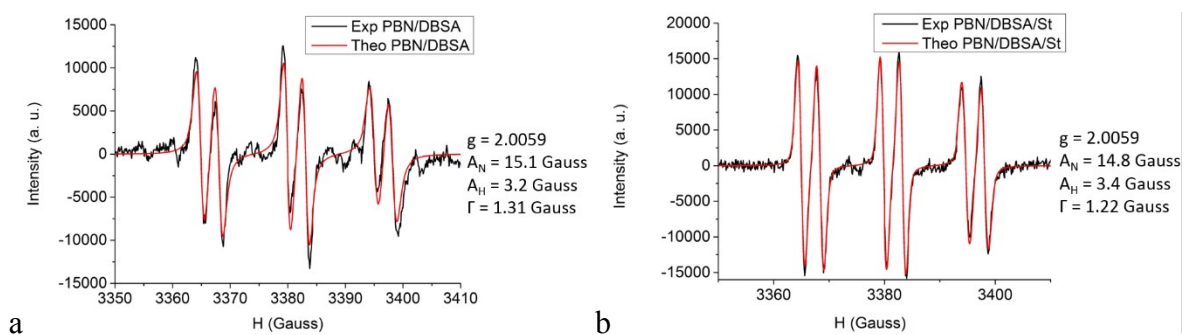**Figure S10** MALDI-ToF mass spectrum of the polymer synthesized using the LASC system (Exp. 1)

Figure S11 Superimposition of the experimental and calculated spectra for (a) the aqueous solution containg hb-DBSNa and (b) the microemulsion containing hb-DBSNa and St
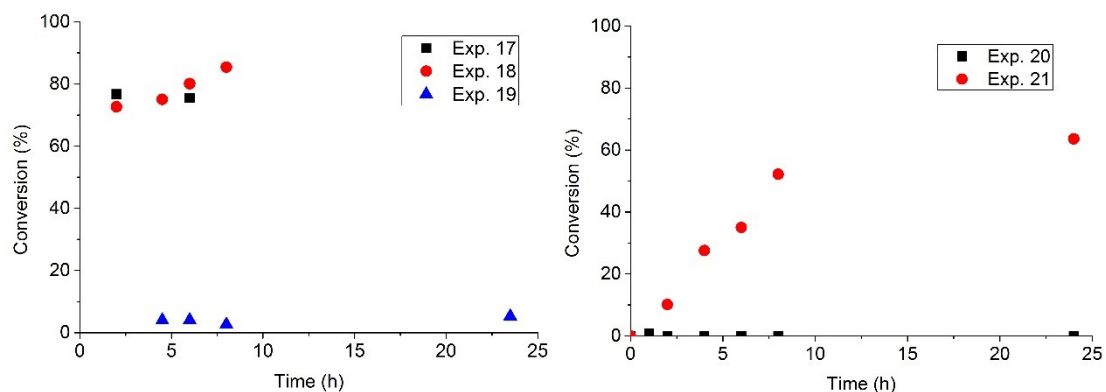

Figure S12 Evolution of the conversion versus time for (left) the experiments 17 to 19 (all reactants, without metal and without surfactant, respectively) using hb-DBSNa as surfactant and (right) the experiments 20 and 21 (all reactants and without metal) using l-DBSNa as surfactant.

(1)   Kosswig, K. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH, 2000.