Heterogeneous Catalysis

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A Catalyst Platform for Unique Cationic (Co)Polymerization in Aqueous Emulsion**

Irina V. Vasilenko, Hui Yee Yeong, Marco Delgado, Samira Ouardad, Frédéric Peruch, Brigitte Voit, François Ganachaud, and Sergei V. Kostjuk**

Dedicated to Professor P. Sigwalt on the occasion of his 90th birthday

Abstract: *Sodium dodecyl benzene sulfonate (DBSNa) surfactants, with a polydisperse and hyperbranched structure, combined with different rare earth metal salts generate highly water-dispersible Lewis acid surfactant combined catalysts (LASCs). This platform of new complexes promotes fast, efficient cationic polymerization of industrially relevant monomers in direct emulsion at moderate temperature. The process described here does not require high shearing, long polymerization time, or large catalyst content. It allows the reproducible generation of high-molar-mass homopolymers of pMOS, styrene, and isoprene, as well as random or multiblock copolymers of the latter two, in a simple and straightforward one-pot reaction.*

Cationic polymerization in aqueous emulsion or suspension is believed to solve the main problems of conventional cationic polymerization, that is, the necessity to work at low temperatures and under strictly anhydrous conditions.[1] Different generations of catalysts have been tested over the last 15 years, most of which were shown to efficiently polymerize *p*-methoxystyrene (*p*MOS).[2] $Yb(OTf)_3$ was the first water-tolerant Lewis acid successfully used to catalyze the slow (several days) cationic polymerization of *p*MOS in aqueous suspension[3] or emulsion at 30 °C.[4] Apart from *p*MOS, only isobutyl vinyl ether could be polymerized under similar conditions[3a,5] but with limited reproducibility.[6] Such lack of reactivity was attributed to the complete dissociation of the $Yb(OTf)_3$ salt in water with the formation of a hydrated Yb cation,[7] which is a weak Lewis acid. Styrene,[8] cyclopentadiene,[9] isoprene,[10] and even acrolein[11] polymerizations were performed in aqueous suspension and/or emulsion for the first time using a singular Lewis acid, $B(C_6F_5)_3$, which does not decompose in water.[12] Despite obvious progresses in terms of reaction rates, the molar masses of synthesized polymers were still not higher than 3000 $g\,mol^{-1}$, a limit value above which interfacial polymerization ceases.[1] $M(C_6F_5)_3$ (M = Al, Ga)[13] or more complex aromatic boranes (C_6F_4-1,2[$B(C_6F_5)_2$],[14] C_6F_4-1,2[$B(C_{12}F_8)_2$])[15] successfully polymerized isobutylene[13–15] and styrene[15] into high-molar-mass polymers (M_n = 10–100 $kg\,mol^{-1}$). Unfortunately, these catalysts required the use of highly concentrated electrolyte aqueous solutions as reaction media, allowing polymerizations exclusively at very low temperatures (below −40 °C).[13–15] These conditions are clearly not those of the conventional emulsion technique, as presented here.

Complexes of Lewis acids with surfactants, so-called Lewis acid surfactant combined catalysts (LASC*s*), were first developed by Kobayashi et al.[16] as excellent catalysts for a great number of organic reactions in aqueous media. D'Agosto et al.[17] followed Kobayashi's work to prepare LASC from ytterbium salts and the simple commercial surfactant sodium dodecyl sulfate. The obtained complexes were, however, soluble neither in water nor in the monomer, and thus did not catalyze polymerization. The use of ytterbium complexed with bulky electrosteric anionic surfactants generated water-dispersible LASC.[18] In very strict conditions, high-molar-mass poly(*p*MOS) (40 $kg\,mol^{-1}$) could be prepared in a noncontrolled fashion. Some difficulties to extract the polymer from this soapy mixture as well as the observed slow polymerization (about 10 days) and long inhibition periods (ca. 100 h), limited the system; in addition, the application of this particular LASC was restricted only to the polymerization of *p*MOS. In this communication, we present a new platform of water-dispersible LASCs precisely prepared from polydisperse and branched (so-called hard) DBSNa surfactants and rare earth metal salts, which success-

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[*] Dr. I. V. Vasilenko, Dr. S. V. Kostjuk
Research Institute for Physical Chemical Problems of the Belarusian State University
14 Leningradskaya st., 220030 Minsk (Belarus)
E-mail: kostjuks@bsu.by

Dr. H. Y. Yeong, Prof. Dr. B. Voit
Leibniz-Institut für Polymerforschung Dresden e.V.
Hohe Strasse 6, 01069 Dresden e.V. (Germany)

Dr. M. Delgado, Dr. F. Ganachaud, Dr. S. V. Kostjuk
INSA-Lyon, IMP, CNRS, UMR5223
20 Boulevard Einstein, 69621 Villeurbanne (France)
E-mail: francois.ganachaud@insa-lyon.fr

Dr. S. Ouardad, Dr. F. Peruch
Laboratoire de Chimie des Polymères Organiques
UMR 5629 CNRS/UB1/IPB University of Bordeaux
16 avenue Pey Berland, 33607 Pessac Cedex (France)

Prof. Dr. B. Voit
Organic Chemistry of Polymers, Technische Universität Dresden
01062 Dresden e.V. (Germany)

Dr. F. Ganachaud
Université de Lyon
69003 Lyon (France)

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fully catalyze the rapid cationic polymerization of various monomers of academic and industrial interest.

Sodium dodecyl benzene sulfonate (DBSNa) is the most abundant surfactant used worldwide in, for example, washing powders. Different generations of this surfactant exist on the market:[19] the first generation of so-called hard surfactants, are highly branched, polydisperse molecules whereas soft DBSNa are mostly bearing narrowly distributed linear alkyl chains. Their solubility in water is generally total at usual concentrations (typically less than 10^{-1} M) but the latter family often requires heating to accelerate their solubilization.[19] In an initial systematic approach in which we tested a large variety of various grades of DBSNa surfactants (see Table S1 for the full list), we stumbled on a specific grade that very easily solubilized in water.

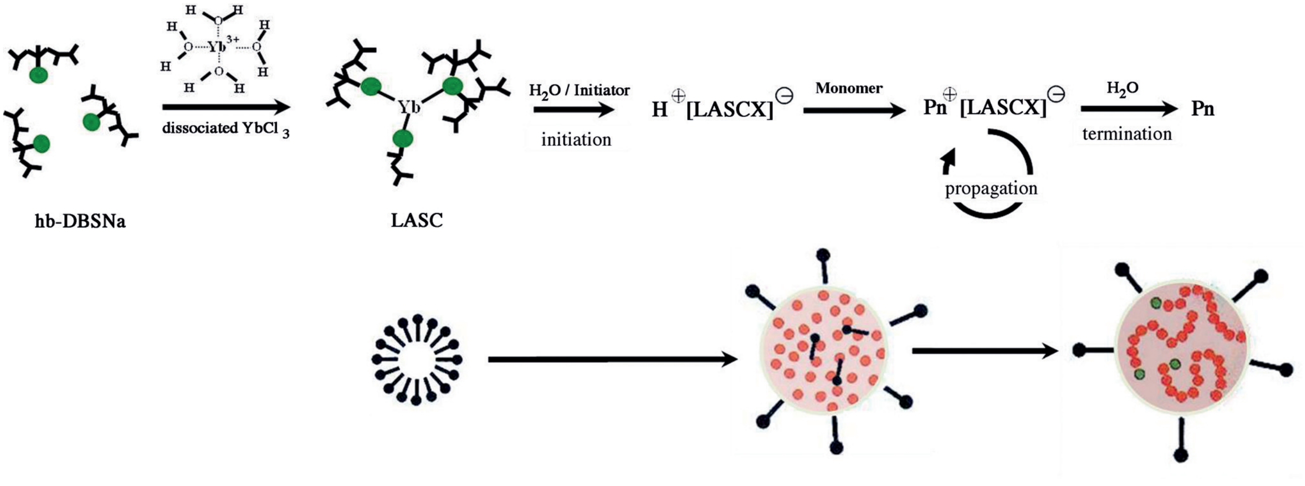
This hb-DBSNa (hyperbranched surfactant) is made of a mixture of polydisperse branched mono- and disubstituted hydrocarbonated isomers, whereas commonly available DBSNa are mainly composed of the *para*-substituted predominantly linear isomer. The polydispersity of hb-DBSNa alkyl chains allows an efficient packing as micelles and thus a fast and total solubilization in water (Scheme 1);[20] besides, upon addition of $YbCl_3$, the LASC complex thus formed generates micelles in small size aggregates (typically around 10 nm, Scheme 1 and Figure S1). On the opposite, the linear surfactants were not able to generate a water-miscible LASC, as shown before,[4b,c,17] but, in the best cases, formed emulsions of about half a micron (Figure S1; see Figures S2–S5 for characterizations of both surfactants).[21]

After preparation of the LASC by adding H_2O (3.5 g) to a mixture of the rare earth metal salt (0.21 g for $YbCl_3 \times 6H_2O$) and hb-DBSNa (0.78 g), the addition of monomer under gentle stirring produces a milky dispersion with an average particle size of around 400 nm. The droplets are formed in absence of high shearing, as long as a slight excess of surfactant is introduced. Monomers with different reactivities (e.g. *p*MOS, styrene, and isoprene) were systematically converted into high-molar-mass polymers, as summarized in

Table 1: Emulsion cationic polymerization of *p*-methoxystyrene (*p*MOS), styrene, and isoprene catalyzed by water-dispersible LASCs.[a]

	Monomer	T [°C]	t [h]	Conv. [%]	M_n [kg mol^{-1}]	M_w/M_n	styrene/isoprene [%][g]	T_g [°C]
1	*p*MOS	60	17	95	29.7	2.1	n.a.	–[h]
2[b]	*p*MOS	60	17	84	11.0	1.7	n.a.	–[h]
3[c]	*p*MOS	60	14	100	36.5	2.1	n.a.	104
4[d]	*p*MOS	50	48	88	19.8	2.2	n.a.	–[h]
5[e]	*p*MOS	40	72	92	20.8	2.5	n.a.	–[h]
6	styrene	50	2.5	94	117.2	3.1	n.a.	–[h]
7	styrene	40	13	95	182.0	3.6	n.a.	102
8[f]	styrene	40	3.5	74	82.0	3.6	n.a.	–[h]
9[b]	styrene	40	24	71	20.6	1.9	n.a.	–[h]
10	isoprene	40	13	89	97.0	3.8	n.a.	−58
11[b]	isoprene	40	24	92	60.8	2.7	n.a.	−57
12	styrene/isoprene (50:50)	40	15	100	124.9	4.9	47:53	6
13	styrene/isoprene (25:75)	40	15	64	81.7	3.9	26:74	−16
14	styrene/isoprene (75:25)	40	15	89	152.2	3.2	73:27	0, 64

[a] Polymerization conditions: H_2O (3.5 g); monomer (1.5 mL); $YbCl_3 \times 6H_2O$ (0.21 g); hb-DBSNa (0.78 g); [b] C_6Cl_5OH (0.14 g) as initiator; [c] H_2O (3.0 g); *p*MOS (2.0 mL). [d] $InCl_3$ (0.12 g); [e] $ScCl_3 \times 6H_2O$ (0.14 g); [f] $Y(NO_3)_3 \times 6H_2O$ (0.21 g); [g] Determined by ^1H NMR spectroscopy; [h] Not measured. n.a. = not applicable.



Scheme 1. Chemistry (top) and physical chemistry (bottom) of the process presented here. Hyperbranched polydisperse DBSNa, upon interaction with $YbCl_3$, generates a LASC complex that micellizes in water and after monomer addition, promotes a stable emulsion. The polymerization starts after a given inhibition period for the catalytic system formation, or directly if an initiator is introduced. Propagation proceeds inside the droplets to generate polymers of high-molar-mass, terminated by hydroxy groups (in green on the scheme). Note that linear DBSNa generates a non-water-dispersible LASC that thus does not promote polymerization (not shown). X = OH or C_6Cl_5O (initiator: H_2O or C_6Cl_5OH, respectively); P_n and P_n^+—terminated and growing polymer chain, respectively.

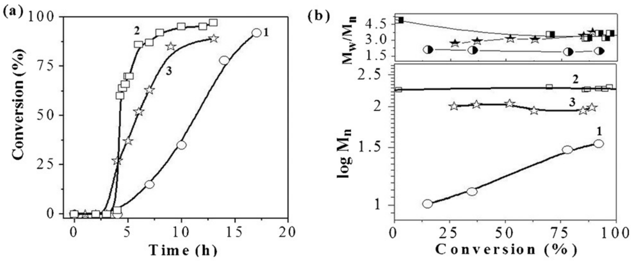


Figure 1. a) Conversion versus time and b) log M_n and M_w/M_n vs. conversion dependences for LASC-mediated cationic polymerization of *p*MOS (1), styrene (2), and isoprene (3) under optimized conditions: $YbCl_3 \times 6\,H_2O$ 0.21 g; hb-DBSNa 0.78 g; H_2O 3.5 g; monomer 1.5 mL. Temperature: 60 °C (*p*MOS) and 40 °C (styrene, isoprene).

Table 1. Figure 1a shows typical kinetic features of the representative polymerization experiments for each monomer. Basically, polymerization of *p*MOS proceeded with an inhibition period of ca. 4 h, and was completed in less than a day at 60 °C. It was proved that polymerization did not start in the absence either of $YbCl_3$ or surfactant (not shown) and that an optimal molar ratio of DBSNa to $YbCl_3$ was 4:1 (Figure S6). Molar mass average increases with conversion reaching the value of about 30 kg mol^{-1} (Figures 1b and S6). Some additional studies revealed that the rate of reaction does not significantly depend on the monomer concentration, whereas M_n increased with increasing pMOS concentration (Figure S7). On the contrary, both the induction period and molar mass decreased with increasing strength of the acid formed by the decomposition of corresponding salt (HOTf > HNO_3 > HCl; Figure S8). Other salts also catalyze the polymerization; for instance, LASCs prepared using ytterbium salts are inactive toward the polymerization of *p*MOS at temperatures lower than 60 °C (Table S1), whereas the polymerization is efficient at 50 °C with $InCl_3$ and 40 °C with $ScCl_3$ (Table 1). The higher catalytic activity of Sc and In salts in comparison with other rare earth metal salts was similarly observed in some organic reactions.[22]

Aiming at extending the scope of using the LASC in the cationic polymerization of vinyl monomers in aqueous emulsion, the (generally sluggish) polymerization of styrene was then investigated. Remarkably, the polymerization of styrene proceeded at faster rate than that of *p*MOS: high monomer conversions (≈95 %) were achieved within only 2.5 h at 50 °C and 13 h at 40 °C, respectively (Table 1, Figure 1).[23] Moreover, the final molar masses of polystyrenes were significantly higher than those of *p*MOS (M_n = 80–190 kg mol^{-1}), whereas MWD was slightly broader (Table 1).[24] This is the highest molar mass ever reported for the cationic polymerization in aqueous media[8] (and even in solution[25]) at such "high" polymerization temperature. The observed difference in the polymerization behaviors may be due to the fact that styrene is less polar than *p*MOS and, therefore, contains less water inside the monomer droplets. This leads to a decrease of the rate of irreversible termination by H_2O which opens, in turn, an access to higher-molar-mass polymers. Another explanation is to be found in the large difference in propagation rate constants of these two monomers ($k_{p,\mathrm{styrene}} \approx 10^9$, while $k_{p,p\mathrm{MOS}} \approx 10^4$–$10^5$ L mol^{-1} s^{-1}).[26]

LASC-mediated emulsion cationic polymerization of isoprene, a monomer hardly polymerized by cationic means into high M_n polymers,[27] was also studied.[28] Isoprene polymerizes quicker than *p*MOS but slower than styrene, whereas molar masses of poly(isoprene)s were found to be between those of polystyrene and poly(*p*-methoxystyrene) (Table 1, Figure 1). Similarly to styrene, the polymerization of isoprene can be achieved at lower temperatures (40 or 50 °C)[29] (Table 1). The synthesized polymers are characterized by relatively low T_g values (T_g from −55 °C to −58 °C; Figures 2a and S9) indicating that most of the double bonds in the chains remain intact (> 94 % by ^{1}H NMR spectroscopy, Figure S10). Besides, the occurrence of relatively broad but monomodal MWD (Figure 2a) evidences that branching occurs under these conditions. The polymer microstructure analyzed by ^{1}H and ^{13}C NMR spectroscopy (Figure S10) revealed predominantly *trans*-1,4- (72 %) and *cis*-1,4-units (21 %), whereas 1,2- and 3,4-structures were present only as minor components (4 and 3 %, respectively), in agreement with the cationic polymerization mechanism.[10]

Several features observed in previous works[2,18] and reproduced here further advocate for a cationic polymeri-

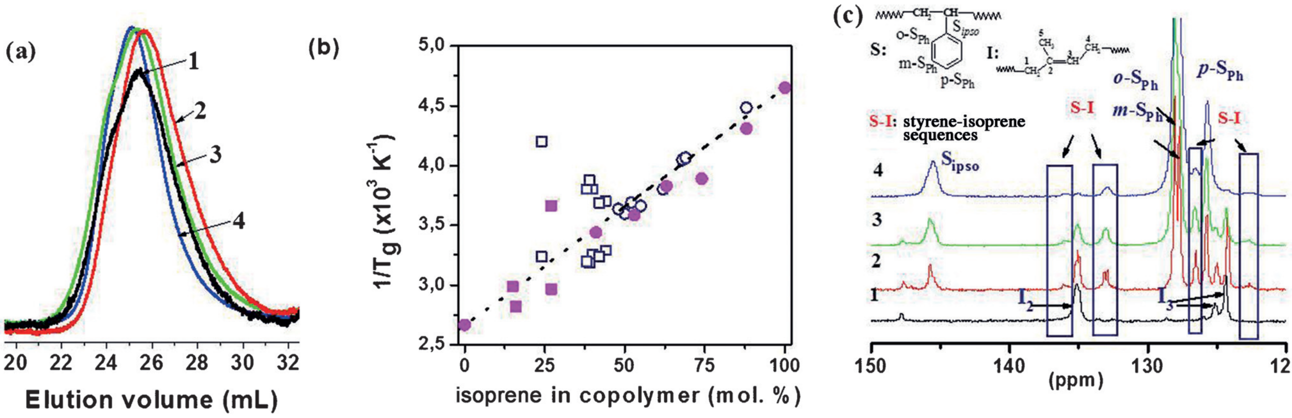


Figure 2. a) SEC curves of polyisoprene (**1**) and copolymers of isoprene with styrene with different styrene content: styrene/isoprene = 26:74 (**2**); styrene/isoprene = 47:53 (**3**) and styrene/isoprene = 73:37 (**4**); b) Fox plot for T_g's obtained in this work (●, ■) and Visseaux's team[30] by metallocene polymerization (○, □) (the dot line is the fit of Fox equation with T_g's of 102 and −58 °C for polystyrene and polyisoprene, respectively); c) olefinic part of ^{13}C NMR spectra (for detailed assignments see Figure S13).

zation process. 1-(4-Methoxyphenyl) ethanol (*p*MOS-OH), an initiator in $B(C_6F_5)_3$-mediated cationic polymerization,[2] does not initiate the polymerization of *p*MOS (Table S2, Figure S11). On the other hand, the addition of this compound to styrene or isoprene polymerization led to a strong decrease of the reaction rate and M_n (entries S17, S18, and S21 in Table S2). This behavior was attributed to the increase of water content in the monomer droplets due to the addition of this quite polar molecule, leading to faster termination with H_2O and the formation of shorter polymer chains.[8] Besides, pentachlorophenol, a weak Brønsted acid ($pK_a = 4.5$) which does not initiate the polymerization by itself, was previously shown to initiate the LASC-mediated polymerization of *p*MOS, as confirmed presently (Figure S11).[18] Here again, for all monomers, the addition of C_6Cl_5OH suppressed the induction period, favored higher initial reaction rate, while strongly decreasing M_n and MWD (Table 1).

Based on the obtained results, a mechanistic scheme can be proposed (Scheme 1). The polymerizations are noncontrolled for all monomers studied here: chains, once initiated by proton (limiting step) grow quickly (loose ion pair) and terminate through the few H_2O molecules present in the core of the monomer droplets. All reactions proceed in the core of monomer droplets/polymer particles, which excludes the occurrence of interfacial polymerization that would lead to oligomeric products. The observed increase of M_n with conversion in case of *p*MOS is consistent with the decrease of H_2O content inside monomer droplets while forming some hydrophobic polymer in the course of reaction. The polarity of monomer versus polymer (and in turn the content of H_2O in droplets) indeed govern the M_n variations of synthesized polymers.

We finally present the successful copolymerization of styrene and isoprene (Tables 1 and S3). Statistical copolymers with monomodal MWD (Figure 2a) and single T_gs (Figure 2, S12) were obtained at styrene/isoprene molar ratios below 75:25. The copolymers synthesized at larger molar ratios, however, showed two T_gs (Figures 2b and S12), the lower one for isoprene-rich blocks, the higher one ascribed to styrene-rich blocks. Such characteristics are the signature of thermoplastic elastomers (for comparison, see data on styrene-isoprene copolymers in Figure 2b obtained by glove-box metallocene chemistry).[30] The structure of synthesized copolymers was also confirmed by ^1H and ^{13}C NMR spectroscopy (Figures 2c and S13), whereas their composition was calculated from ^1H NMR spectra (Figure S13).

In summary, we have demonstrated a powerful, sustainable procedure to generate homopolymers and copolymers of unique microstructure by cationic polymerization. The key point is the choice of the surfactant so as to generate submicronic emulsions and promote cationic polymerization. The synthesis of optimized DBSNa surfactant is under way.

Keywords: heterogeneous catalysis · isoprene · Lewis acids · polymerization · styrene

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[27] Only low M_n products ($< 5000\ \text{g mol}^{-1}$) with broad, multimodal MWD and loss of unsaturation were typically obtained by cationic polymerization of isoprene even at low temperatures.

[28] With the example of the polymerization of isoprene, we checked that LASC can be successfully recovered (see Table S4) and reused. Polymerization of isoprene under the same conditions as in entry 10 (Table 1) gave the following results: conversion = 74 %; $M_n = 72.6\ \text{kg mol}^{-1}$; $M_w/M_n = 3.4$.

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