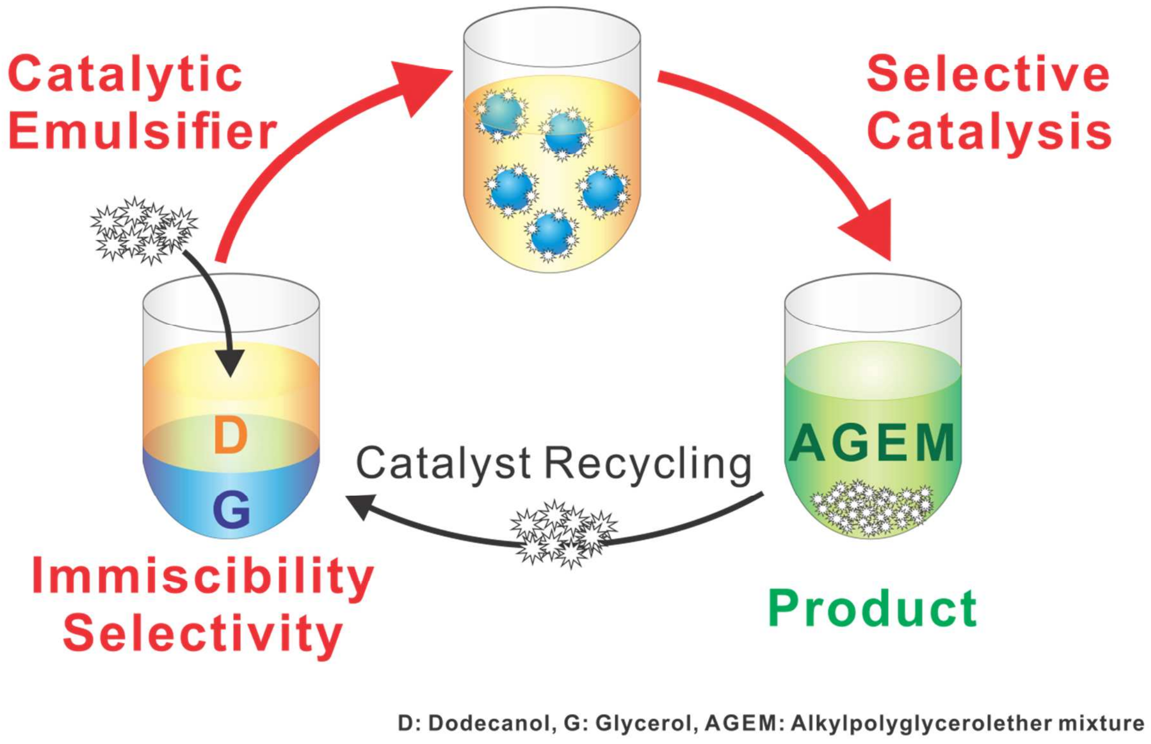
Green Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem



One sentence highlight:

A new strategy for biobased surfactant preparation through Pickering interfacial catalytic process of glycerol and dodecanol with bi-functional catalyst.

Preparation of Bio-based Surfactant from Glycerol and Dodecanol through Direct Etherification

Zhaoyu Fan,[a,b] Yan Zhao,[b] Florentina Preda,[b] Jean-Marc Clacens,[b] Hui Shi,[b] Limin Wang,[a*] Xiaoshuang Feng,[b*] and Floryan De Campo[b]

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

In this paper, we studied an original synthetic strategy to prepare bio-based surfactants through direct solvent free etherification of glycerol with dodecanol using heterogeneous interfacial acidic catalysts dubbed Pickering Interfacial Catalysis (PIC). The conversion of dodecanol could be achieved to 60-71% with limited production of didodecyl ether (DE) as the main side product. The selectivity of the final product, alkylpolyglycerylether (AGEM) could be pushed to > 80% with water removal process at 150 °C, as a mixture of monolaurylpolyglyceryl ethers, multilaurylpolyglyceryl ethers and multilauryl cyclicpolyglyceryl ethers. AGEM could be isolated with a suitable work-up and were fully characterized by GC (MS), HPLC, SFC/HRMS etc. The physicochemical properties of these new surfactants were evaluated as well as their laundry performances. This solvent-free direct etherification process paves the way towards new value-added applications of glycerol.

1. Introduction

Surfactants are widely utilized in industry and daily life. Their global production is estimated over 12 million metric ton per year with an annual growth of 3-4%.[1,2] Today, surfactants are still produced mainly from fossil-based raw materials and very few products are fully bio-based. However, global environmental challenges have fueled a growing demand for sustainable surfactants with acceptable cost and performance.[3-6] One possible solution is to use glycerol as an alternative hydrophilic building block to replace ethylene oxide for the production of nonionic surfactants, which can then be 100% bio-based when we choose alkyl chains from bio-based resources (such as lauryl alcohol from coco oil). Indeed, ester-based mono- and diglycerides, prepared by the transesterification of triglycerides with excess glycerol and base catalyst, represent the main glycerol-based surfactants in the market.[7] However, their application is somehow limited due to the limited hydrolytic stability of ester bonds. Therefore, ether-linked surfactants obtained from glycerol and hydrophobic carbon chains would be preferred by formulators. Alkyl polyglyceryl ether had been recognized as nonionic surfactants with greater solubilizing and emulsifying abilities than alkoxylates.[8]

From the surfactant point of view, surface active reagents with different hydrophilic lipophilic balance (HLB) values are applied in different fields but they embody both hydrophobic and hydrophilic moieties. As shown in Scheme 1, two immiscible phases (dodecanol and glycerol) react to obtain hetero-ethers (Monododecyl polyglyceryl ether, MAGEn) or homo-ethers (didodecyl ether, DE; Polyglycerol, PG). MAGEn could react further with dodecanol to generate multidodecyl polyglyceryl ether. All these dodecyl polyglyceryl ethers are surface active reagents. Therefore, the derivation of dodecanol would be only two directions: dodecyl polyglyceryl ethers as surfactant or DE as main hydrophobic by-product. For this reaction, the key for optimization is to reach as low as possible the DE selectivity while maintaining a high dodecanol conversion in order to make an efficient use of dodecanol, a big cost contributor.

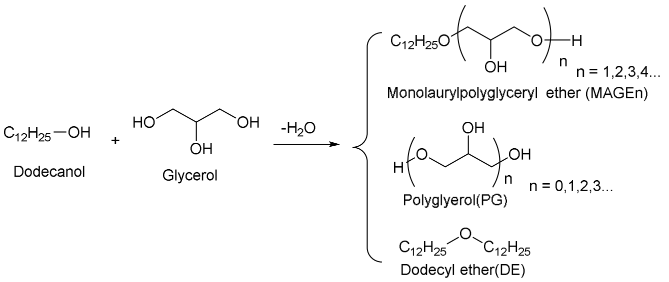
With the rapid development of biodiesel, glycerol has become widely available as by-product (10 wt%) from transesterification of triglycerides.[9-12] As a result, new processes are needed for the conversion of glycerol to value added products to support the development of biorefinery and oleochemical industries.[5,13] Etherification from glycerol could be achieved efficiently with light active olefins[4,14-18] affording products that could be used as fuel additives. Unfortunately, the direct etherification of glycerol or polyglycerol with long alkyl chains (≥ 8 carbons) for surfactant preparation remains a significant challenge to date. Typically, activated equivalents of glycerol such as ketal,[19] epichlorohydrin[20] or glycidol[21-24] are used to achieve satisfactory yields due to the low reactivity and poor selectivity of glycerol. However, such processes and reagents have serious environmental and safety issues due to their toxicity or the generation of salts. More recently, Lemaire group managed to prepare glycerol ethers directly from aldehyde or acids under reducing conditions with (di, tri) glycerol in the presence of an acid.[25-28] The same strategy was also successful for the reductive alkylation of glycerol with fatty acid methyl ester (biodiesel). However, the yields were low for longer alkyl chains (41% yield for C12 alkyl chain)[29].

The direct etherification between glycerol and aliphatic alcohol is also of great interest because of the low cost of aliphatic alcohol and glycerol. Most of reported works are focused on direct etherification of glycerol with active or light alcohols.[30-37] Very few examples have covered the direct reaction of glycerol with long-chain aliphatic alcohol.[38,39] Weckhuysen group reported the direct etherification of bio-based polyols with long-chain olefins under heterogeneous

Table 1 Comparative reaction results performed under different catalytic conditions[a]

Entry	Catalyst	Catalyst (mol%)	Conv. Of Dodecanol (%)	Yield of DE (%)	Selectivity to DE (%)	Yield of MAGE (%)[d]	Selectivity to MAGE (%)	Mass balance of C12 chain (%)[e]
1	PTSA	5	66	29	44	7	11	55
2	DBSA	5	90	46	51	16	18	69
3	PTSA+SiO_2-TM[b]	5	67	24	36	9	13	49
4	PTSA+SiO_2-C_{40}[c]	5	72	25	35	10	14	49

[a] Reaction conditions: Glycerol (3.68 g, 0.04 mol), dodecanol (1.86 g, 0.01 mol), 150 °C, 16 h with 1 wt% silica particles added for entries 3, 4. The data in this table was calculated based on GC analysis results. [b] Silica nanoparticles grafted with trimethyl. [c] Silica nanoparticles grafted with polystyrene with M_n with 40 K. [d] MAGE The total amount of MAGE1, MAGE2 and MAGE3. MAGE1: Monododecylglyceryl ether. MAGE2: Monododecyldiglyceryl ether. MAGE3: Monododecyltriglyceryl ether. [e] The traceable dodecyl chain (DE and MAGE) by GC to the total converted dodecanol.



Scheme 1 Direct etherification of dodecanol and glycerol.

acidic catalysis, good results were obtained for diols[40] . However, low conversion (~ 20%) was given in the case of glycerol.[41,42] The high viscosity and hydrophobicity of glycerol give difficulties to solve and interact with hydrophobic substrates resulting in a miscibility issue. In addition, selectivity issue was caused by the homo- or hetero- etherification of alcohol, glycerol and their products due to hydroxyl groups in these compounds. Pouilloux and Jerome reported the synthesis of monododecylglyceryl ether (MAGE1) with dodecanol and glycerol using dodecyl benzenesulfonic acid (DBSA, 20mol%) as surfactant-type catalyst.[38] The miscibility and selectivity issues were presented by the low yield of MAGE1 (30%) and high selectivity (55%) to didodecyl Ether (DE) as a by-product.

Therefore, the two challenges are miscibility and selectivity for the direct etherification between dodecanol and glycerol to produce dodecyl polyglyceryl ethers. To favor the hetero-etherification in such immiscible system, the ideal way is to make the reaction occur at their interface to limit the homo-etherification of reactants with themselves. We propose a concept of Pickering Interfacial Catalysis (PIC) with catalyst particles used as emulsifier for Pickering emulsion of biphasic system (dodecanol and glycerol).[43] Emulsions were borrowed to boost the reactivity and yield by increasing the contact of reactants or by isolating the product for different immiscible systems, including solid stabilized emulsion, named as Pickering emulsion.[44 ,45] Using particles as catalyst gives the possibility to recycle them in order to achieve very low cost. Additionally, we hope the location of such catalysts at interface could provide synergetic effects to make the etherification selectively occur between dodecanol and glycerol, avoiding the homo-etherification of dodecanol or glycerol themselves.

To realize the PIC strategy, we selected polymer of styrene and its grafted silica particles as materials for the bi-functional catalysts. The polymerization and sulfonation of styrene (St) are well studied with very good control of polymerization and broad knowledge on characterization and properties.[46] The amphiphilicities of copolymers with styrene and styrene sulfonic acid (SSA) can be easily tuned based on their compositions of polystyrene (PSt) and polystyrene sulfonic acid (PSSA) from controlled synthesis.

In this contribution, we make a first report of surfactant synthesis based on the direct etherification of glycerol and dodecanol with co-polymer of PSt/PSSA. The catalytic activities were investigated by the copolymer compositions of PSt/PSSA with tunable amphiphilicity controlled by their sulfonation degree. Hybrid silica particles grafted with those amphiphilic copolymer were also prepared to address the catalyst recyclability issue. The products were fully characterized, and their physicochemical properties were measured as surfactants.

2 Results and discussion

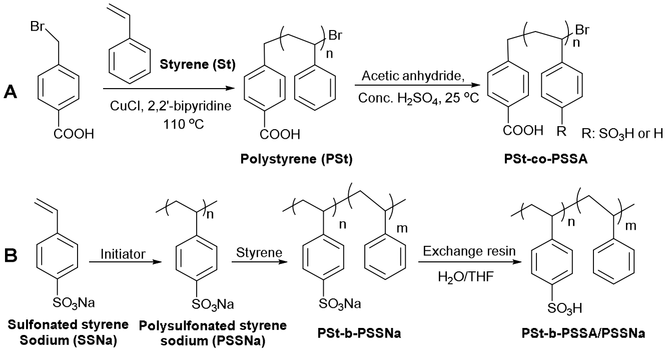
2.1 Preparation of catalysts

First, preliminary results were obtained to explore the distributive effect of homogeneous catalysts in immiscible phases (see Table 1). In our repeated reaction with DBSA as catalyst, DE selectivity was 51% with most of dodecanol converted (90%). Possessing similar acidic strength, *p*-tolunesulfonic acid (PTSA) with more affinity to glycerol than DBSA, gave lower DE selectivity and lower dodecanol conversion. These effects come from the distribution difference of DBSA and PTSA in dodecanol/glycerol. To improve the interaction between the two immiscible phases, two silica nanoparticles without catalytic sites were introduced to generate the Pickering emulsion of dodecanol/glycerol with PTSA as catalyst for the study of emulsion effects. As shown in Table 1, the two particles were silica nanoparticles grafted with trimethyl (SiO_2-TM, 1.6 wt%, Thermal Gravity Analysis, TGA) and polystyrene (SiO_2-C_{40}, 37.2 wt%, TGA). Comparing to the

Table 2 Main characteristic data of synthesized sulfonated random and block polystyrenes

Entry	Type	Sample Name[a]	No.of St and SSA/SSNa (PSt, M_n by NMR, Kg mol^{-1})	Polymer M_n (NMR) (Kg mol^{-1})	PSt or PSSNa M_n (GPC)/PDI (Kg mol^{-1})	Sulfonation mol% by ^1H NMR	Sulfonation mol% by titration[b]	Acidity (mmol g^{-1}) by titration
1	PSt-co-PSSA	$RC_{211}S_{21}$	211 (22.0)	25.6	26.6/1.20	21	21	1.7
2		$RC_{211}S_{30}$	211 (22.0)	26.9	26.6/1.20	29	30	2.3
3		$RC_{211}S_{40}$	211 (22.0)	28.4	26.6/1.20	38	40	2.9
4		$RC_{211}S_{53}$	211 (22.0)	30.6	26.6/1.20	51	53	3.6
5		$RC_{211}S_{56}$	211 (22.0)	31.0	26.6/1.20	53	56	3.7
6		$RC_{115}S_{32}$	115 (12.0)	14.9	12.5/1.25	31	32	2.4
7		$RC_{115}S_{51}$	115 (12.0)	16.7	12.5/1.25	51	51	3.5
8	PSt-b-PSSNa/PSSA	$BC_{46}S_{50}$	46.2	7.7[c]	6.5/1.27	68[d]	50	3.5

[a] R: random, B: block, Cx: number of St, SSA(SSNa). Sx: sulfonation degree of styrene by titration. [b] Values calculated from the acidity by titration. [c] Molecular value of PSt-b-PSSNa/PSSA obtained with sulfonation degree by ^1H NMR based on the chain length of PSSNa (M_n = 6500 g mol^{-1}) detected by GPC. [d] ^1H NMR measurements were done at 67 °C for better solubility. PDI: Poly Dispersity Index.



Scheme 2 Synthetic routes of amphiphilic copolymers PSt-co-PSSA and PSt-b-PSSNa/PSSA.

results with PTSA, there was no increase on dodecanol conversion but reduced slightly the DE selectivity. Based on these results, we believe that bi-functional PIC catalysts could be a good solution for the immiscibility and selectivity issues. To adapt to this oil/oil biphasic system, block and random amphiphilic copolymers based on PSt and PSSA were systematically synthesized and evaluated.

2.1.1 Sulfonated polystyrene

Two types of copolymers (as shown in Scheme 2) were prepared through controlled methodology in order to investigate the catalytic activity on their structures and amphiphilicity. Random sulfonated polystyrene copolymer (PSt-co-PSSA) was synthesized following a standard atom transfer radical polymerization (ATRP) procedure with 4-(bromomethyl) benzoic acid as initiator.[47] Two samples were composed with an average molar mass of 12500 g mol^{-1} and 26600 g mol^{-1} for comparison. Subsequently, PSt-co-PSSA samples with desired sulfonation degrees were obtained by mixing PSt with the calculated amounts of acetic anhydride and sulfuric acid in 1,2-dicholoroethane.[48]

For block polymer of polystyrene and polystyrene sulfonic acid (PSt-b-PSSNa/PSSA), sodium polystyrene sulfonate (PSSNa) was prepared through nitroxide mediated polymerization with TEMPO and $K_2S_2O_8/Na_2S_2O_5$ in mixture of ethylene glycol, water (ethylene glycol: water = 4:1 v/v). The obtained polymer (M_n = 6500 g mol^{-1}) was further polymerized with St under the same conditions adapted from references to give block polymer (PSt-b-PSSNa).[49-51] At the end, PSt-b-PSSNa was stirred with a hydrogen exchange resin in mixed solvent of water and tetrahydrofuran (THF) to yield a partially protonated block polymer PSt-b-PSSNa/PSSA.

The characterization data of seven random and one block polystyrene samples were listed in Table 2. Random sulfonated polystyrene samples (PSt-co-PSSA) covered the acidity from 20 to 60 mol%, while keeping two PSt chain lengths [Table 2 column 4, Molecular weight (M_n) = 22 and 12 Kg mol^{-1} representing 211 and 115 St units respectively][45] for comparison. The M_n was characterized by both GPC and NMR for the homopolymers (PSt or PSSNa) as first block (Table 2 column 4, 6). The mean values of M_n by NMR were in good agreement with the results of GPC. The M_n of final polymers was calculated from the M_n of first block and their sulfonation degree by NMR (Table 2 column 5). In comparison with PSt-co-PSSA, the values of sulfonation degree of PSt-b-PSSNa/PSSA obtained from NMR and titration were not matching, even performed at higher temperature (67 °C)[52] to improve the solubility. Due to the incomplete proton exchange, the sulfonation degrees determined by titration were lower than that expected value from NMR, especially in the cases of higher extents of PSSNa, as shown in Table 2 columns 7-8. The acidity values, verified from 1.7 to 3.7 mmol g^{-1} were applied to the catalyst loading calculation for reaction implementation.

2.1.2 Polymer coated silica nanoparticles

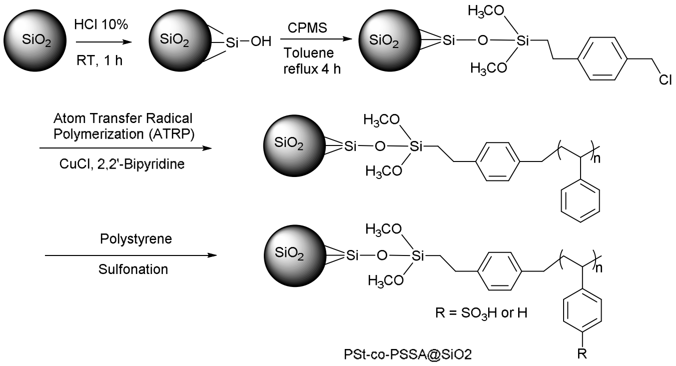
Silica nanoparticles grafted with PSt-co-PSSA were synthesized (Scheme 3) following the classical procedures.[53-59] The activated silica nanoparticles[37] were first etherified with [(Chloromethyl)phenylethyl] trimethoxysilane (CPMS, mixed *m, p* isomers), the ether bonds of grafted initiator moiety chlorobenzene assure the stability for the subsequent catalysis in harsh reaction conditions. PSt chain was extended through

ATRP of styrene in bulk. The PSt grafted silica nanoparticles were subsequently submitted to sulfonation under mild conditions. All silica nanoparticles were dispersed in water and freeze dried after the last step to avoid aggregation. Three samples with different sulfonation degree were prepared with characterization data listed in Table 3.

Table 3 Main characteristics of the polystyrene grafted silica particles (PSt-co-PSSA@SiO_2)

Entry	Item	SiO_2-A[d]	$SC_{46}S_{42}$[e]	$SC_{46}S_{59}$	$SC_{46}S_{90}$
1	Mean particle radius (DLS, nm)	64	75	79	74
2	BET surface (m^2 g^{-1})	190	37	2.6	1.5
3	Grafting degree (wt%) with CPMS by TGA	-	5.7	5.7	5.7
4	CPMS or SiOH groups (per nm^2)[a]	3.7	0.65	0.65	0.65
5	Weight uptake (200-900 °C) (%)[b]	1.1	42	51	55
6	PSt backbone M_n (g mol^{-1})/Number of St[a]	-	4800/46	4800/46	4800/46
7	Sulfonation (molar % / polystyrene)[c]	-	42	59	90
8	Acidity (mmol g^{-1}, Titration)	-	1.2	1.8	2.7

[a] Value measured and calculated from TGA (Fig. S1). [b] For parent silica particles, the weight loss temperature range is 400-900 °C. [c] Average value calculated from titration. [d] parent silica particles without any surface modification used as starting material for the grafting process. [e] S: silica nanoparticles, Cx: number of styrene, Sx: sulfonation degree of PSt.



Scheme 3 Synthesis of PSt-co-PSSA grafted on silica nanoparticles (PSt-co-PSSA@SiO_2).

The results showed the CPMS weight loss was 5.7 wt% by TGA measurement. Further calculation showed only 0.65 of 3.7 OH groups per nm^2 were connected by CPMS (Table 3 entries 3-4). The specific surface area decreases sharply from 190 to 1.5 m^2 g^{-1} with the increase of sulfonation degree (Table 3 entry 2) probably due to the coverage of PSt chains at silica surface and silica particles aggregation. The PSt chain length calculated from TGA was 4800 g mol^{-1} and the weight loss of PSt-co-PSSA@SiO_2 varied from 42 to 55% (Table 3 entry 5) while keeping similar particle size (74-79 nm as shown in Table 3 entry 1). The sulfonation degrees of polystyrene were 42-90 mol% while acidity of sulfonated polystyrene grafted silica samples changed from 1.2 to 2.7 mmol g^{-1} (Table 3, entries 7-8).

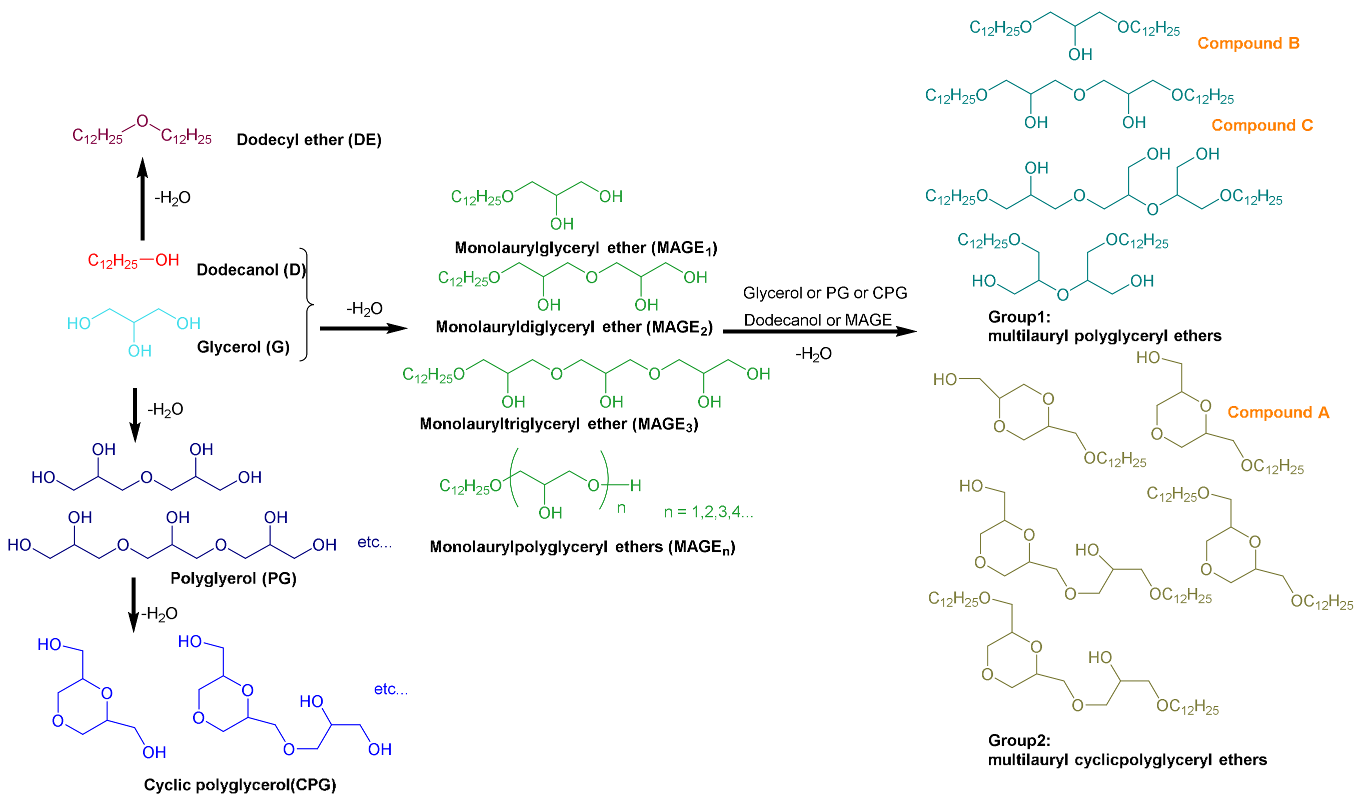
2.2 Activity of catalyst for etherification

Before studying the catalytic results of Pickering interfacial catalysts, their interfacial behaviors in the glycerol/dodecanol biphasic system were firstly investigated. Interfacial tensions measurements and micrographic study of emulsion droplets were performed on both the amphiphilic polymers and the silica particles to prove their location at interface. As shown in Fig. S2, the interfacial tension between dodecanol/glycerol was reduced at different levels for all samples including SiO_2-TM, SiO_2-C_{40}, $RC_{211}S_{53}$, $BC_{46}S_{50}$ and $SC_{46}S_{59}$. The micrographic pictures (Fig. S3) at 30min after emulsification showed the droplet sizes were at < 1 μm to 20 μm. These results indicated particles or polymers were indeed located at the interface which stabilized the glycerol or dodecanol droplets. The interfacial etherification between glycerol and dodecanol could then be favorably catalyzed by these bifunctional amphiphilic polymers or their grafted silica particles.

For the etherification reaction, as we stated in the introduction, the dodecanol conversion and the DE selectivity are the two important factors for the evaluation of catalyst performance. Gas chromatogram (GC) was employed to evaluate the catalytic performance by tracking the derivatives of dodecanol. The conversion of dodecanol, yield and selectivity of surface active product and DE, were chosen as performance indexes for catalysts at different sulfonation degree and feeding ratios. Here, the yield and selectivity of surface active product were calculated from all the surface active components including MAGEn and its derivatives (group1 and group2 as shown in Scheme 4).

2.2.1 Catalytic activity with amphiphilic copolymers

Random and block sulfonated copolymers with different amphiphilicity as listed in Table 2 were screened in our target etherification reaction in order to understand the influence of the copolymer composition and structures on their catalytic activity under the Pickering Interfacial Catalysis. To minimize the production of DE and improve the performance of product as a surfactant, excess of glycerol to dodecanol was fed in the reaction. All experiments were performed under the reaction conditions: 1:4 molar ratio of dodecanol to glycerol, under static vacuum (200 mbar) for 24 h at 150 °C. The reaction results are listed in Table 4. For PSt-co-PSSA, the sulfonation degree changes the DE yield and selectivity. As shown in Table 4, entries 1-5, the DE selectivity was limited to < 16% when the sulfonation degree of catalyst was higher than 40%. When the sulfonation reaches 50%, the selectivity to DE is



Scheme 4 Representative structures of possible components inside dodecanol and glycerol etherification mixtures.

When the sulfonation reaches 50%, the selectivity to DE is decreased to 4.9%. Overall, between 40% and 60% of sulfonation degree, the copolymers possess amphiphilic balance that gives a good selectivity to surface active product and DE.

To understand the effect of amphiphilicity, reaction results were plotted following the catalyst sulfonation degree. As shown in Fig. 1A, the high sulfonation degree of catalysts helped to reach low DE selectivity but the dodecanol conversion shrank significantly. The catalysts with high sulfonation degree are more hydrophilic, which prefer to locate in glycerol phase whatever the polymer chains were stretching or curling. Consequently, the preferred location of catalyst in glycerol phase reduced the homo-etherification of dodecanol to obtain low DE selectivity while decreasing the dodecanol conversion. Therefore, the catalyst amphiphilicity is the key to keep low DE selectivity. Interestingly, the chain length of polymer PSt-co-PSSA at screening range gives no remarkable effect on the catalytic results (entries 2, 5 and 7, 8 in Table 4).

The screening of catalyst loading showed that 0.08-0.1 eq. addition of PSt-co-PSSA is a good ratio to keep high catalytic efficiency (Fig. 1B). Similarly, catalytic performance catalyzed by PSt-b-PSSNa/PSSA was also investigated, as shown in Table S1. Catalyst load at 0.05 eq. is the best option without any concern of gel or solidification in the reaction system due to the instability of PSSA block under reaction conditions.[60] Generally, random copolymer PSt-co-PSSA has similar performance with block copolymer PSt-b-PSSNa/PSSA. In addition to slightly better selectivity to surface active products, easier synthetic accessibility and stability make random copolymers a better choice than block ones.

It could be noted that the conversions of dodecanol were quite low (< 20%) despite of high surface active products selectivity in the cases of reaction catalyzed by high sulfonated copolymers. To push the reaction to high conversion, the produced water as by-product was removed efficiently with special designed glassware, which collected and trapped water for separation during the process. The results are listed in Table 4, entries 6 and 10. As expected, low selectivity of DE (< 16%) was obtained the same as the reactions without water removal. Furthermore, the conversions of dodecanol were pushed to > 60% with good selectivity and moderate yield of surface active products by these amphiphilic copolymers.

2.2.2 Catalytic activity with polymer grafted silica particles

As discussed in chapter 2.2.1, PSt-co-PSSA has similar catalytic performance with PSt-b-PSSNa/PSSA with an easier synthesis process. So a series of PSt-co-PSSA grafted silica particles (PSt-co-PSSA@SiNP) were synthesized as shown in Scheme 3, in order to tackle the recyclable issue of polymers. These hybrid catalysts were all tested with water removal under the same conditions; their catalytic results are listed in Table 4, entries 11-13. The same as PSt-co-PSSA catalysts, higher sulfonation degree led to a better surface active products selectivity but a lower dodecanol conversion. The surface active product yields remained at ~ 50%, which was similar to copolymers.

Table 4 Summarized PIC etherification results obtained with different amphiphilic bifunctional catalysts[a]

Entry	Catalyst	Catalyst quantity (Acidity/Dodecanol, eq.)	Conv. of D (%)	Yield of Surface active products (%)	Selectivity to Surface active products (%)	Yield of DE (%)	Selectivity to DE (%)
1	RC$_{211}$S$_{21}$	0.10	79	43	54	36	46
2	RC$_{211}$S$_{30}$	0.10	57	33	59	24	41
3	RC$_{211}$S$_{40}$	0.10	42	35	84	7	16
4	RC$_{211}$S$_{53}$	0.10	24	21	88	3	12
5	RC$_{211}$S$_{56}$	0.10	19	18	95	1	5
6	**RC$_{211}$S$_{56}$-WR**[b]	**0.10**	**60**	**53**	**90**	**6**	**10**
7	RC$_{115}$S$_{32}$	0.10	56	39	69	17	31
8	RC$_{115}$S$_{51}$	0.10	19	18	94	1	6
9	BC$_{46}$S$_{50}$	0.08	18	16	93	1	7
10	**BC$_{46}$S$_{50}$-WR**	**0.05**	**68**	**57**	**84**	**11**	**16**
11	SC$_{46}$S$_{42}$-WR	0.05	71	46	65	24	35
12	**SC$_{46}$S$_{59}$-WR**	**0.05**	**61**	**48**	**78**	**13**	**22**
13	SC$_{46}$S$_{90}$-WR	0.05	63	52	83	11	17
14	**SC$_{46}$S$_{59}$-WR$_1$**[c]	**0.05**	**55**	**43**	**79**	**12**	**21**
15	**SC$_{46}$S$_{59}$-WR$_2$**	**0.05**	**49**	**38**	**77**	**11**	**23**

[a] Reaction conditions: 1:4 molar ratio of dodecanol to glycerol, under static vacuum (200 mbar) for 24 h at 150 °C by vigorous stirring at nitrogen atmosphere. [b] WR Reactions done with water removal. [c] WR$_1$ and WR$_2$: First and second recycling of SC$_{46}$S$_{59}$.

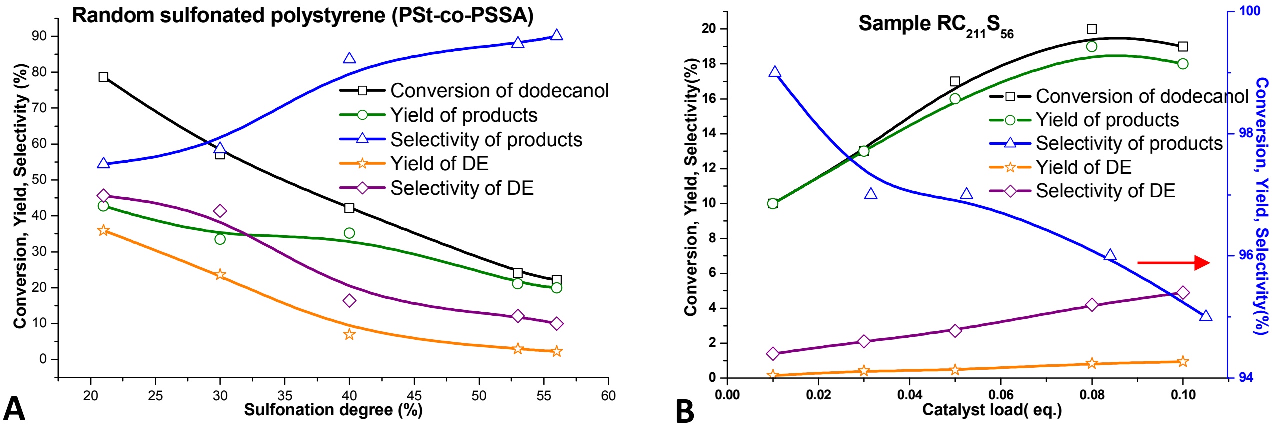


Fig. 1 Profiles of reaction results (conversion of dodecanol, yields and selectivities to surface active products and DE) as a function of sulfonation degree and catalyst loading. **A**: The sulfonation degree screening based on random sulfonated polystyrene (RC$_{211}$ series); **B**: Catalyst load optimization with sample RC$_{211}$S$_{56}$.

In this case, sample SC$_{46}$S$_{59}$ has the similar catalytic performance with sample SC$_{46}$S$_{90}$. The reduction of catalyst loading from 0.05 eq. to 0.02 eq. decreased quickly the dodecanol conversion and the surface active products yield while keeping similar surface active products selectivity. Overall, PSt-co-PSSA@SiNP series showed similar performance to PSt-co-PSSA catalysts with very slight decrease of surface active product selectivity. The reason might be the change of catalyst location at the dodecanol/glycerol interface due to the solidification of PSt-co-PSSA. Then, recycling experiments were performed with SC$_{46}$S$_{59}$ as listed in Table 4, entries 14-15. The dodecanol conversion decreased from 61% to 49% after two recycling, while keeping almost the same selectivity. The surface active products yield went down from 48% to 38%. We have to mention such polymer grafted silica particles could not be totally recovered from reaction system due to its nano-scaled size and amphiphilicity although being settled down with high speed centrifugation. They were not very stable at the reaction conditions according to the TGA profiles before and after reaction. The two reasons resulted in the catalytic activity decrease during catalysts recycle process.

2.3 Characterization of reaction mixture

As mentioned in chapter **2.2**, the reaction was evaluated by monitoring the derivation of dodecyl carbon chain. For better comparison of the catalytic activities, we simplified the yield and selectivity of surface active products to be the sum of all the derivatives from dodecanol except DE. Actually, the analysis of dodecanol derivatives with glycerol is a big challenge due to the polyhydroxyl structures of glycerol and its cyclization[46,61] . There are hundreds of structures, which makes it impossible to prepare all the references and separate them by any chromatograph. Peaks of dodecanol, DE, MAGE1, MAGE2 and MAGE3 can be detected by GC but they shared only part of dodecyl chain comparing to the total conversion of dodecanol. There is a big gap on the dodecyl chain mass balance from the converted dodecanol (Table 1, column 7-9).

To understand the disagreement between converted dodecanol and dodecanol derivatives detected by GC, ^{1}HNMR was employed to characterize all the dodecyl groups that were not decomposed after reaction with biphenyl as the internal standard. The peaks a, b and c that appeared at 0.77, 1.16, and 1.42 ppm respectively were ascribed to the methyl, methylene protons of dodecyl groups as shown in Fig. S4. The rest methylene group connected to oxygen that appeared at 3.5 ppm was overlapped by the signal of glyceryl protons. No unsaturated and aldehyde protons were detected, and the integration ratio of peaks a:b:c is 3:18:2, indicating the full detection of dodecyl group under the reaction condition. The quantities of dodecyl and glyceryl units were quantified by NMR with the internal standard, which proved again that the dodecyl groups remain unchanged after reaction.

Therefore, other dodecanol derivatives should exist but they can't be detected or identified by GC. The possible further reactions of MAGEn with dodecanol and glycerol are listed in Scheme 4. Besides dimerization of MAGEn and dodecanol, intramolecular etherification could be favored to form cyclic dioxane derivatives. To verify this hypothesis, compound A and B of the dimerized MAGE1 and dodecanol, compound C of the cyclic MAGE2 were synthesized and analyzed by GC as representative compounds. The structures of compound A, B， C is shown in Scheme 4. Gas Chromatogram coupled with Mass Spectrometer (GC/MS) was also employed to confirm their identities by mass spectroscopy (see Fig. S5 for the typical profiles and mass spectra). All the compounds appeared at roughly same retention time for both GC and GC/MS as shown in Fig. S6. The good agreement of retention time and mass spectra illustrated the entity of dimerization and cyclization. Such types of cyclic and substituted derivatives were also detected by Weckhuysen in the case of synthesis to the long alkyl chain ethers through direct etherification between glycerol and 1-octene.[41 ,42] In their work, the reaction condition used was 140 °C under acidic media, which is quite similar to our reaction conditions.

To further understand the surface active products composition after etherification, the mixture was analyzed by Supercritical Fluid Chromatogram equipped with high resolution mass detector (SFC/HRMS). The profile was shown in Fig. 2. Although the formulas could be deduced from the accurate mass values, it's a big challenge to assign an exact structure to every mass peak due to the complexity caused by many kinds of hydroxyls from glyceryl units. However, the number of dodecyl group, glyceryl units and dehydrated water could be deduced based on etherification rule. The explanation results from main peaks were shown in Fig. S7. Peaks were assigned with the following formula: nD + mG – xH_2O, where D and G represent dodecanol and glycerol respectively and x is the molar value of water removed to form the detected compound. If x = n + m - 1, the formed compound has the acyclic structures, ex: D + G - H_2O (MAGE1), D + 3G - 2H_2O (MAGE3), 2D + 3G - 4H_2O. If x > n + m - 1, the compound is formed with cyclic structure due to intramolecular dehydration. Ex: D + 2G - 3H_2O; or polycyclic D + 4G - 5H_2O. For more details, please refer to Fig. S7.

These compounds were assigned into three groups: monododecyl (poly)glyceryl ethers (MAGEn), multideodecyl (poly)glyceryl ethers and multideodecyl cyclic (poly)glyceryl ethers (Scheme 4). All of them are composed of hydrophilic (glyceryl) and lipophilic (dodecyl) groups, essentially surface active reagents. From this point of view, the dodecyl derivatives except dodecyl ether are all regarded as surfactants, although they have different HLB values. As explained,

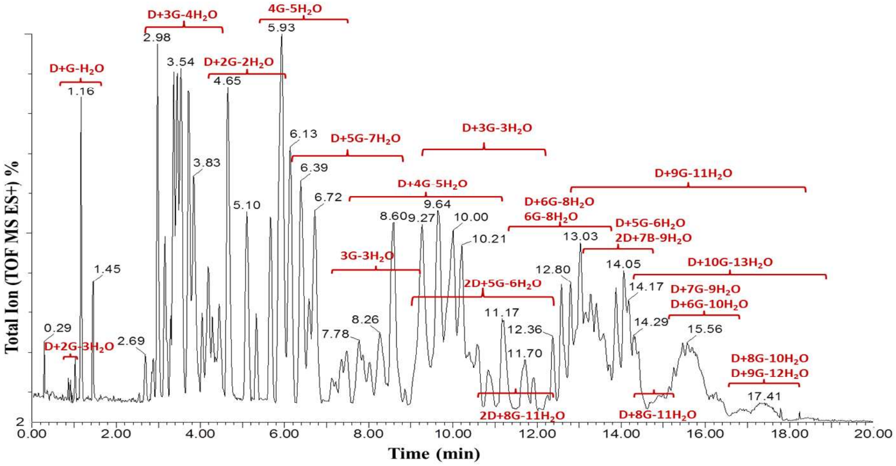


Fig. 2 Typical SFC/HRMS profile of one representative sample AGEM1. D: dodecanol, G: glycerol.

plenty of detected compounds inside the mixture were over dehydrated. Although we can't quantify the composition, cyclic derivatives from intramolecular etherification may explain the big gap of mass balance of dodecanol in this reaction.

2.4 Physicochemical properties and application performance of surface active product

As discussed in chapter **2.3**, the reaction mixture is a mixture of starting materials, product, by-product including glycerol, dodecanol, PG, DE, MAGEn and its derivatives. All the dodecyl derivatives except DE are regarded as surfactant product [Alkyl(poly)glyceryl ether mixture, AGEM]. This is a new surfactant without any physico-chemical understanding available.

One purification procedure was adopted to obtain the product for further characterization and potential application as surfactant. Catalyst, most of glycerol and its oligomers were removed through precipitation in a mixture of THF/diethyl ether. Other impurities contained in organic portion could be removed under vacuum distillation (for dodecanol), and through washing with heptane from methanol solution of the mixture after distillation. Three representative surfactant samples were thus obtained and their composition data are listed in Table 5. All of the samples after workup contained very low contents of dodecanol and DE. Glycerol and its oligomers were 12, 13, 14 wt% separately, which don't affect the performance of surfactants generally as they are water soluble. For samples AGEM1 and AGEM2, the contents of MAGE1, MAGE2 were quite low but they took more than 35 wt% in AGEM3.

As mentioned, the quantities of dodecyl and glyceryl units were quantified by NMR with internal standard, which gave us the molar ratio of glyceryl/dodecyl. If we eliminate the contribution of DE, dodecanol and glycerol, the effective molar ratio of glyceryl to dodecyl could be approximately calculated as following Eq:

$$\text{Effective molar ratio of } \frac{\mathrm{G}}{\mathrm{D}} = \frac{(\mathrm{G_{NMR}} - \mathrm{G_{PG}})}{(\mathrm{D_{NMR}} - \mathrm{D_{dodecanol}} - \mathrm{D_{DE}})}$$

Where, $\mathbf{G_{NMR}}$ is the mole of total glyceryl units from quantitative NMR; $\mathbf{G_{PG}}$ is the mole of glyceryl units from polyglycerol(PG) by HPLC analysis; $\mathbf{D_{NMR}}$ is the mole of total dodecyl units from quantitative NMR; $\mathbf{D_{dodecanol}}$ and $\mathbf{D_{DE}}$ are respectively the moles of dodecyl units from dodecanol and DE based on GC analysis results.

As shown in Table 5, the three samples have the effective molar ratios of G/D to be 3.4, 3.2 and 1.4 for AGEM1, AGEM2 and AGEM3 with surfactant active content of 80%, 86% and 86% respectively as the active content. AGEM1 and AGEM2 were prepared with 1:6 molar ratio of D/G while 1:4 molar ratio of D/G was used for AGEM3. We can see that effective molar ratio of G/D is tunable to provide wide HLB value, which means that the product can be tuned according to application requirement. Following the analytical characterization, these representative samples from our process were compared regarding their surface active properties with traditional benchmarks of alkyl polyethoxylate ether (AEO7) and monoalkyl polyglyceryl ether (MAGE4)[62] . Their main characteristics were listed in Table 6.

Table 5 Composition of final surface active product after purification

Entry	Sample name	Active content (wt%)[c]	Effective molar ratio of G/D	Glycerol (PG) wt%[d]	Dodecanol (wt%)[e]	DE (wt%)[e]	MAGE1 (wt%)[e]	MAGE2 (wt%)[e]
1	AGEM1[a]	80	3.4	14	4.0	1.7	1.6	2.1
2	AGEM2[a]	86	3.2	12	1.7	0.48	6.2	1.9
3	AGEM3[b]	86	1.4	13	0.71	ND	29	6.6

[a] The samples were prepared with 1:6 molar ratio of dodecanol/glycerol, 10% molar acid functions/dodecanol, under static vacuum, 24 h, 150 °C. [b] The sample was prepared with 1:4 molar ratio of dodecanol/glycerol, 10% molar acid functions/dodecanol, under static vacuum, 24 h, 150 °C. [c] Active content was calculated: Active content (wt%) = 100% − glycerol(PG)% − dodecanol% − DE%. [d] by HPLC analysis. [e] by GC analysis.

Table 6 Main characteristics of AGEM products compared to AEO7 and MAGE4 as benchmarks

Entry	Sample name	CMC ($\mathrm{g\ L^{-1}}$)	ST at CMC ($\mathrm{mN\ m^{-1}}$)	Foam(mm) at 2.5 $\mathrm{g\ L^{-1}}$	Cloud point (°C)	Solubility(1% aqueous solution at r.t)	Laundry performance
1	AGEM1	0.068	28	117	38-40	Slightly turbid	130
2	AGEM2	0.057	28	105	31-35	Slightly turbid	118
3	AGEM3	NA	NA	67	<0	Turbid	78
4	AEO7	0.023	32	143	46-48	clear	155
5	MAGE4	0.024	31	150	>95	clear	138

MAGE4 Monoalkylpolyglyceryl ether with number of glyceryl unit at 4 as an average value. AEO7: Laurylpolyethoxylate-7 ether, commercialized product. NA: not available.

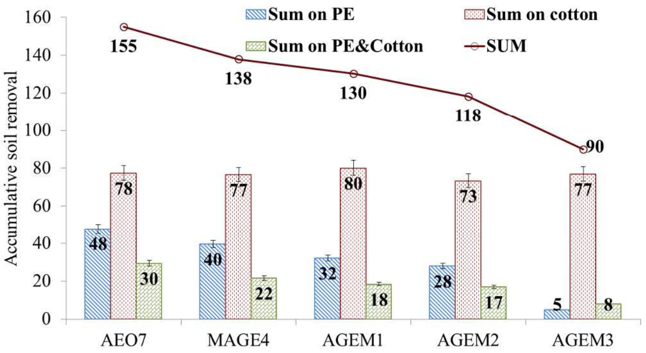


Fig. 3 Laundry performance on polyester (PE), cotton and polyester&cotton (65/35). The stains removal was adjusted based on active content. Polyester&cotton: mixed fabric with 65% polyester and 35% cotton.

Firstly, those typical surfactants physico-chemical properties were compared including critical micelle concentration (CMC), surface tension at CMC, Rossmile foaming height, Cloud point etc. From these results, we can observe that the samples have the same level of CMC with AEO7 and MAGE4-benchmark, while having lower surface tension at CMC.

The aqueous solutions at 1 wt% are slightly turbid possibly due to the dodecanol and DE residue. This could be the reason for the slightly lower Rossmile foam height. The cloud points are lower than the value of MAGE4 but similar with the value of AEO7. Overall, these AGEM samples are comparable with industrial benchmarks although they contain cyclic derivatives of MAGEn and light residues of DE and dodecanol.

Secondly, their laundry performance was evaluated to compare with AEO7 and MAGE4 benchmarks. The results are plotted in Fig. 3. Among all the application that alkylethoxylate provided, their use as cleaning agent for laundry has a big market while strong requirement for green replacement.[62] As shown in Table S2, laundry performance on cotton, polyester and polyester & cotton was measured based on 11 stains, including standard stains from China, USA and Europe.[63] The accumulative stains removal on cotton for AGEM1 was better than AEO7 and MAGE4 although the performance on polyester was a little worse. This brings a shining perspective, considering that cotton is chosen for fabric and cloth more and more today.[64] Overall AGEM samples showed slightly lower accumulative stains removal ratio comparing to AEO7 and MAGE4 as benchmark. In consideration of the effective molar ratio of these samples are 3.2 and 3.4 respectively, we believe samples with better performance can be produced with our adjustable synthetic strategy.

3 Conclusions

A novel green strategy was developed to prepare bio-based surfactants through direct etherification between glycerol and dodecanol with bifunctional amphiphilic catalysts on the dodecanol/glycerol interface. Well-tuned amphiphilic copolymer PSt-PSSA, bearing synergetic effect of emulsifier and catalyst, perform high catalytic activity with a conversion of dodecanol up to 60% and selectivity to product at 90%. Such amphiphilic copolymer grafted on silica provides recyclable catalysts showing similar activities to linear copolymers although the stability and recyclability were not perfectly satisfactory yet. Analytical characterizations with GC (MS), HPLC, SFC/HRMS etc… indicate that the reaction mixture contained 5 series of components including glycerol&PG, dodecanol&DE, MAGEn, multidodecyl (poly)glyceryl ethers and multidodecyl cyclic (poly)glyceryl ethers. Physico-chemical characterization and laundry tests on fabrics of the final surfactants indicate that they are comparable surfactants to benchmarks with low surface tension and good performances on cotton cloth.

Acknowledgements

This research was supported by Solvay China, French CNRS, and the National Science Foundation of China (NSFC) (21272069). The authors would like to thank Mr. Yongwei Xu from Waters Co., Ltd. for the help on SFC/HRMS analysis, Miss Astrid Tay for the measurement of fabric laundry performance, Mrs. Renate Schwiedernoch for the design on graphical abstract.

Notes and references

[a] Key Laboratory of Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Mei Long Rd., Shanghai 200237, PR China.
E-mail: wanglimin@ecust.edu.cn, Tel: +86 21 64253881; Fax: +86 21 64253881

[b] Eco-Efficient Products and Processes Laboratory (E2P2L), UMI 3464 Solvay/CNRS, 3966 Jin Du Rd., Xin Zhuang Industrial Zone, Shanghai 201108, PR China.
E-mail: fxs101@gmail.com, Tel: +86 21 24089416; Fax: +86 21 24089001

Electronic Supplementary Information (ESI) available: experimental part, micrographic pictures, interfacial tension, characterization results. See DOI: 10.1039/b000000x/

1 M. Levison, *Handbook of detergents part F: production*, 2009, **142**, 1-38.
2 G. Reznik, P. Vishwanath, M. Pynn, J. Sitnik, J. Todd, J. Wu, Y. Jiang, B. Keenan, A. Castle, R. Haskell, T. Smith, P. Somasundaran and K. Jarrell, *Appl Microbiol Biot*, 2010, **86**, 1387-1397.
3 P. Foley, A. Kermanshahi Pour, E. S. Beach and J. B. Zimmerman, *Chem Soc Rev*, 2012, **41**, 1499-1518.
4 J. F. Izquierdo, M. Montiel, I. Palés, P. R. Outón, M. Galán, L. Jutglar, M. Villarrubia, M. Izquierdo, M. P. Hermo and X. Ariza, *Renew Sust Energ Rev*, 2012, **16**, 6717-6724.
5 F. Jérôme, Y. Pouilloux and J. Barrault, *ChemSusChem*, 2008, **1**, 586-613.
6 W. G. Haigh and D. J. Hanahan, *Biochimical et Biophysica Acta (BBA)/Lipids and Lipid Metabolism*, 1965, **98**, 640-643.
7 U. Biermann, U. Bornscheuer, M. A. Meier, J. O. Metzger and H. J. Schäfer, *Angew Chem Int Edit*, 2011, **50**, 3854-3871.
8 H. Sagitani, Y. Hayashi and M. Ochiai, *J Am Oil Chem Soc*, 1989, **66**, 146-152.
9 M. Ayoub and A. Z. Abdullah, *Renew Sust Energ Rev*, 2012, **16**, 2671-2686.

10 A. B. Leoneti, V. Aragão-Leoneti and S. V. W. B. de Oliveira, *Renew Energ*, 2012, **45**, 138-145.

11 C. A. G. Quispe, C. J. R. Coronado and J. A. Carvalho Jr, *Renew Sust Energ Rev*, 2013, **27**, 475-493.

12 H. W. Tan, A. R. Abdul Aziz and M. K. Aroua, *Renew Sust Energ Rev*, 2013, **27**, 118-127.

13 Y. Zheng, X. Chen and Y. Shen, *Chem Rev*, 2008, **108**, 5253-5277.

14 W. Zhao, B. Yang, C. Yi, Z. Lei and J. Xu, *Ind Eng Chem Res*, 2010, **49**, 12399-12404.

15 J. A. Melero, G. Vicente, G. Morales, M. Paniagua, J. M. Moreno, R. Roldán, A. Ezquerro and C. Pérez, *Appl Catal A-gen*, 2008, **346**, 44-51.

16 K. Klepáčová, D. Mravec, A. Kaszonyi and M. Bajus, *Appl Catal A-gen*, 2007, **328**, 1-13.

17 M. D. González, P. Salagre, E. Taboada, J. Llorca, E. Molins and Y. Cesteros, *Appl Catal B-environ*, 2013, **136-137**, 287-293.

18 F. Frusteri, L. Frusteri, C. Cannilla and G. Bonura, *Bioresource Technol*, 2012, **118**, 350-358.

19 K. Urata and N. Takaishi, *J Surfactants Deterg*, 1998, **1**, 73-82.

20 K. Urata, S. Yano, A. Kawamata, N. Takaishi and Y. Inamoto, *J Am Oil Chem Soc*, 1988, **65**, 1299-1302.

21 Y. Sakanishi and N. Muraoka, DSM IP Assets B.V. US 8153728, 2012.

22 S. Berkowitz, FMC Corporation, US 4298764 A, 1981.

23 V. Istratov, H. Kautz, Y. K. Kim, R. Schubert and H. Frey, *Tetrahedron*, 2003, **59**, 4017-4024.

24 A. M. Hofmann, F. Wurm and H. Frey, *Macromolecules*, 2011, **44**, 4648-4657.

25 M. Sutter, W. Dayoub, E. Métay, Y. Raoul and M. Lemaire, *ChemSusChem*, 2012, **5**, 2397-2409.

26 Y. Shi, W. Dayoub, G. R. Chen and M. Lemaire, *Sci China Chem*, 2010, **53**, 1953-1956.

27 Y. Shi, W. Dayoub, G. R. Chen and M. Lemaire, *Green Chem*, 2010, **12**, 2189-2195.

28 Y. Shi, W. Dayoub, A. Favre-Réguillon, G. R. Chen and M. Lemaire, *Tetrahedron Lett*, 2009, **50**, 6891-6893.

29 M. Sutter, W. Dayoub, E. Métay, Y. Raoul and M. Lemaire, *Green Chem*, 2013, **15**, 786-797.

30 G. D. Yadav, P. A. Chandan and N. Gopalaswami, *Clean Tech Environ Policy*, 2012, **14**, 85-95.

31 F. Liu, K. De Oliveira Vigier, M. Pera-Titus, Y. Pouilloux, J. M. Clacens, F. Decampo and F. Jérôme, *Green Chem*, 2013, **15**, 901-909.

32 M. D. González, Y. Cesteros and P. Salagre, *Appl Catal A-gen*, 2013, **450**, 178-188.

33 J. S. Chang and D. H. Chen, *J Taiwan Institute Chem Eng*, 2011, **42**, 760-767.

34 J. Janaun and N. Ellis, *J Appl Sci*, 2010, **10**, 2633-2637.

35 F. Frusteri, F. Arena, G. Bonura, C. Cannilla, L. Spadaro and O. Di Blasi, *Appl Catal A-gen*, 2009, **367**, 77-83.

36 K. Klepáčová, D. Mravec and M. Bajus, *Chemical Paper*, 2006, **60**, 224-230.

37 Y. Gu, A. Azzouzi, Y. Pouilloux, F. Jérôme and J. Barrault, *Green Chem*, 2008, **10**, 164-167.

38 P. Gaudin, R. Jacquot, P. Marion, Y. Pouilloux and F. Jérôme, *ChemSusChem*, 2011, **4**, 719-722.

39 P. Gaudin, R. Jacquot, P. Marion, Y. Pouilloux and F. Jérôme, *Catal Sci Tech*, 2011, **1**, 616-620.

40 A. N. Parvulescu, P. J. C. Hausoul, P. C. A. Bruijnincx, R. J. M. Klein Gebbink and B. M. Weckhuysen, *Catal Today*, 2010, **158**, 130-138.

41 A. N. Parvulescu, D. Mores, E. Stavitski, C. M. Teodorescu, P. C. A. Bruijnincx, R. J. M. K. Gebbink and B. M. Weckhuysen, *J Am Chem Soc*, 2010, **132**, 10429-10439.

42 A. M. Ruppert, A. N. Parvulescu, M. Arias, P. J. C. Hausoul, P. C. A. Bruijnincx, R. J. M. Klein Gebbink and B. M. Weckhuysen, *J Catal*, 2009, **268**, 251-259.

43 Z. Y. Fan, A. Tay, M. Pera-Titus, W. J. Zhou, S.Benhabbari, X. S. Feng, G. Malcouronn, L. Bonneviot, F. D. Campo, L. M. Wang and J.-M. Clacens, *J Colloid Interf Sci*, 2014, **427**, 80-90.

44 S. Crossley, J. Faria, M. Shen and D. E. Resasco, *Science*, 2010, **327**, 68-72.

45 J. Faria, M. P. Ruiz and D. E. Resasco, *Adv Synth Catal*, 2010, **352**, 2359-2364.

46 Stephanie Cassel, Catherine Debaig, Thierry Benvegnu, Patrick Chaimbault, Michel Lafosse, Daniel Plusquellec and a. P. Rollin, *Eur J Org Chem*, 2001, **2001**, 8752896.

47 *Please refer to supporting data for the synthesis of polymer and its grafted silica nano-particles.*

48 B. Keoshkerian, M. Georges and D. Boils-Boissier, *Macromolecules*, 1995, **28**, 6381-6382.

49 F. Niepceron, B. Lafitte, H. Galiano, J. Bigarré, E. Nicol and J.-F. Tassin, *J Membrane Sci*, 2009, **338**, 100-110.

50 J. T. Park, J. A. Seo, S. H. Ahn, J. K. Kim and S. W. Kang, *J Ind Eng Chem*, 2010, **16**, 517-522.

51 J. Ding, C. Chuy and S. Holdcroft, *Macromolecules*, 2002, **35**, 1348-1355.

52 M. Bouix, J. Gouzi, B. Charleux, J. P. Vairon and P. Guinot, *Macromol Rapid Comm*, 1998, **19**, 209-213.

53 A. Carvalho and A. Curvelo, *Macromol Rapid Comm*, 2003, **36**, 5304-5310.

54 C. Vieira Grossi, E. de Oliveira Jardim, M. H. de Araújo, R. Montero Lago and M. J. da Silva, *Fuel*, 2010, **89**, 257-259.

55 T. von Werne and T. E. Patten, *J Am Chem Soc*, 2001, **123**, 7497-7505.

56 D. Savin, J. Pyun, G. Patterson, T. Kowalewski and K. Matyjaszewski, *Journal of Polymer Science: Part B: Polymer Physics*, 2002, **40**, 2667-2676.

57 M. N. Tchoul, M. Dalton, L. S. Tan, H. Dong, C. M. Hui, K. Matyjaszewski and R. A. Vaia, *Polymer*, 2012, **53**, 79-86.

58 N. Saleh, T. Sarbu, K. Sirk, G. Lowry, K. Matyjaszewski and R. Tilton, *Langmuir*, 2005, **21**, 9873-9878.

59 F. Adam, Osman, H., Hello, K.M., *J Colloid Interf Sci*, 2009, **331**, 143-147.

60 M. L. Di Vona, E. Sgreccia, S. Licocccia, G. Alberti, L. Tortet and P. Knauth, *J Phys Chem B*, 2009, **113**, 7505-7512.

61 Alexander Sunder, Ralf Hanselmann, Holger Frey and R. M. lhaupt, *Macromolecules*, 1999, **32**, 4240-4246.

62 Y. Yu, J. Zhao and A. E. Bayly, *Chinese J Chem Eng*, 2008, **16**, 517-527.

63 I. S. (ICS), *GB/T 13174-2008 and EC 60456-2010* 2008.

64 Y. Mu, *Cotton Textile Tech*, 2002, **11**, 5-10.