# Sustainable Micellar Gold Catalysis – Poly(2-oxazolines) as Versatile Amphiphiles

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Received: February 1, 2016; Revised: March 22, 2016; Published online: April 25, 2016

Dedicated to Prof. Dr. Henning Hopf on the occasion of his 75<sup>th</sup> birthday.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201600139.

**Abstract:** The application of five polymer amphiphiles in the gold-catalyzed allene cycloisomerizations under aqueous micellar conditions is described. The polymers were prepared by ring-opening cationic polymerization based on poly(2-methyl-2-oxazoline) as hydrophilic segment and different hydrocarbon- or fluorocarbon-based hydrophobic segments. The catalytic activity in the gold-catalyzed allene cyclization is strongly dependent on the type of gold precursor, the salt concentration in the bulk aqueous medium, and the concentration of the polymeric am-

# Introduction

Gold catalysis represents a powerful synthetic strategy which is particularly useful in terms of efficiency and selectivity.<sup>[1]</sup> Since gold catalysts are usually nontoxic and many reactions take place under mild conditions, gold catalysis is highly suitable for the development of sustainable synthetic methods. Different approaches were implemented so far to allow catalyst recycling and to reduce the amount of organic solvents. In this context, ionic liquids have to be mentioned because of their excellent solvent properties which enable the transformation of many substrates of different polarity.<sup>[2]</sup> In contrast, the use of water as reaction medium is strongly limited. Water-soluble gold catalysts allow the conversion of polar compounds with potential of catalyst recycling but hydrophobic reactants are more difficult to convert.<sup>[3]</sup> However, if simple gold catalysts are used in water<sup>[3d]</sup> or in an organic solvent,<sup>[1]</sup> recycling is impossible due to phiphile. Best results were obtained with 2 mol% of gold(III) bromide, 1 mM of amphiphile and 5 M sodium chloride, affording over 80% yield for different heterocyclic products. The catalyst system is also suitable for the dehydrative cyclization of acetylenic diols to furans. Moreover, successful catalyst recycling was demonstrated in three consecutive runs when using optimized extraction conditions.

**Keywords:** allene cycloisomerization; gold catalysis; green chemistry; micelles; polymer amphiphiles

a rapid decomposition of the catalyst to metallic gold. Here, the use of micellar catalysis opens a versatile alternative which was rarely used up to now. Particularly vitamin E-based nanomicelles were pointed out as an adequate reaction medium for transition metal-catalyzed coupling reactions<sup>[4]</sup> and also for gold catalysis.<sup>[5]</sup> Polymeric amphiphiles may represent an alternative to low molecular weight surfactants. Their higher structural variability and straightforward synthesis enables versatile strategies and possibilities of fine tuning.<sup>[6]</sup> Previous work has shown that the cationic ring-opening polymerization (CROP) of 2-oxazolines provides an excellent method to synthesize tailormade polymeric nanoreactors, which have been used for transition metal-catalyzed transformations.<sup>[7]</sup> The CROP methodology enables the introduction of functional groups *via* the initiator<sup>[8]</sup> and/or the terminating agent,<sup>[9]</sup> and the diversity of the monomers allows control of the polarity of the polymer from hydrophilic to hydrophobic and fluorophilic.<sup>[10]</sup>

Here, we show for the first time the effect of five different poly(2-oxazoline) amphiphiles in the gold-catalyzed cycloisomerization of functionalized allenes to the corresponding heterocycles under aqueous micellar reaction conditions. Of particular interest is the effect of different salt concentrations on micelle size and on the catalytic activity. Moreover, we studied the effect of micelles with a hydrocarbon core vs. a partly fluorinated core on the gold-catalyzed conversion of fluorinated and non-fluorinated allenic substrates. The catalyst system was also applied to the dehydrative cyclization of acetylenic diols to furans.

## **Results and Discussion**

To explore the influence of fluorinated and non-fluorinated amphiphiles in micellar gold catalysis, five different block copolymers were prepared (Figure 1). The amphiphilic polymers P1-P4 were synthesized via block copolymerization of 2-heptyl-2-oxazoline and 2-methyl-2-oxazoline using methyl triflate (P1, P2), butyl triflate (P3), and 4,4,4-trifluorobutyl tosylate (P4), respectively, as initiators. P5 was synthesized without the addition of 2-heptyl-2-oxazoline because of the hydrophobic character of the initiator 1H,1H,2H,2H-perfluorodecyl tosylate. All polymerizations were terminated by the addition of piperidine. The critical micelle concentration was determined for polymers **P3** ( $cmc = 2 \cdot 10^{-6}$  M) and **P5** (cmc = $1.2 \cdot 10^{-6}$  M) by fluorescence spectroscopy and pyrene solubilization experiments and was in the micromolar range which is typical for such polymers.<sup>[7c,d]</sup>



**Figure 1.** Amphiphilic poly(2-oxazolines) **P1–P5** (red: hydrophobic part; blue: hydrophilic part).

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**Table 1.** Influence of polymeric amphiphile and salt additionon the gold-catalyzed cycloisomerization of allene 1a.

<i>t</i> -Bu,,,,,//	OH 1a	AuBr <sub>3</sub> (5 mol%) amphiphile, NaCl H <sub>2</sub> O, r.t.	- <sub>t-Bu</sub> ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	0 2a OTBS
Entry	Amphiphile	NaCl	Time <sup>[a]</sup>	Yield [%]
1	<b>P1</b> (17 mM)	_	2 d	84
1	<b>P1</b> (5 mM)	_	2 d	84
3	<b>P1</b> (17 mM)	3 M	1 d	78
4	<b>P1</b> (5 mM)	3 M	5 h	80
5	<b>P1</b> (1 mM)	3 M	1 h	87
6	<b>P1</b> (0.5 mM)	3 M	20 min	83
7	<b>P1</b> (0.125 mM)	3 M	10 min	84
8	<b>P2</b> (1 mM)	_	6 h	92
9	<b>P2</b> (1 mM)	3 M	30 min	82
10	PTS (17 mM) <sup>[b]</sup>	_	30 min	80
11	PTS $(10 \text{ mM})^{[b]}$	-	15 min	86
12	PTS (17 mM) <sup>[b]</sup>	3 M	5 min	80

<sup>[a]</sup> Time required for complete conversion of allene **1a**.

<sup>[b]</sup> PTS = polyoxyethanyl- $\alpha$ -tocopheryl sebacate.

To examine the ability of the amphiphiles P1 to P5 to promote the gold-catalyzed cycloisomerization of functionalized allenes under micellar reaction conditions, the conversion of substrate 1a into the corresponding dihydrofuran 2a was chosen as benchmark reaction (Table 1). Similar to the typical procedure for vitamin E-based amphiphiles like polyoxyethanyl- $\alpha$ -tocopheryl sebacate (PTS),<sup>[5]</sup> we started with a polymer concentration of 17 mM for P1. With 5 mol% of AuBr<sub>3</sub>, long reaction times of 2 days were observed, even if a lower polymer concentration of 5 mM was chosen (Table 1, entries 1 and 2). However, prior investigations with PTS or TPGS have shown that the addition of NaCl to the micellar solution can be very beneficial for the process and often leads to an acceleration.<sup>[5a,b]</sup> For this reason, we tested the addition of NaCl (3M) and found a strong rate increase. Using 17 mM of P1 in a 3M NaCl solution, the cyclization was finished after 1 day, while lower polymer concentrations of 5 and 1 mM resulted in shorter reaction times of 5 h and 1 h, respectively (Table 1, entries 3, 4 and 5). Even lower concentrations of the amphiphile (0.5 or 0.125 mM) decreased the reaction times further to 20 and 10 min, but the allene was not completely dissolved anymore (Table 1, entries 6 and 7). Therefore, the investigations were continued with a polymer concentration of 1 mM. Under these conditions, P2 was also tested with and without the addition of NaCl, supporting the hypothesis of a general salt effect (Table 1, entries 8 and 9). For comparison, we also tested PTS and found the same concentration and salt effect on the reactivity (Table 1, entries 10-12). Compared to the polymeric amphiphiles P1 and

**P2**, the cyclization is much faster in PTS-derived micelles; the latter, however, require in general higher concentrations and do not offer the structural flexibility of poly(2-oxazolines). All cyclizations took place with good to very good yields.

To further examine the salt effect, allene **1a** was cyclized under constant conditions using **P2** as amphiphile (2 mol% AuBr<sub>3</sub>, 1 mM **P2**, H<sub>2</sub>O), while increasing the salt concentration systematically. The results are shown in Table 2. While the product was isolated

**Table 2.** Influence of the salt concentration on the cycloiso-merization of allene 1a in the presence of amphiphile P2.<sup>a]</sup>

Entry	NaCl	Time <sup>[b]</sup>	Yield [%]
1	1 M	2 d	80
1	2 M	9 h	91
3	3 M	7 h	87
4	4 M	5 h	81
5	5 M	2.5 h	80
6	7 M	2.5 h	82

<sup>[a]</sup> Conditions: 2 mol% AuBr<sub>3</sub>, 1 mM **P2**.

<sup>[b]</sup> Time required for complete conversion of allene **1a**.

in high yields, the reaction time decreased with higher NaCl concentrations. With 1 M NaCl, a rather long reaction time of 2 days was observed, whereas a 5 or 7 M NaCl solution led to a much shorter time of 2.5 h (Table 2, entries 1, 5 and 6). When 7 M NaCl was used, the solubility of NaCl in water at room temperature reached the limit and excess NaCl precipitated. Thus, a 5 M NaCl solution was used for further investigations.

Next, the activity of different gold catalysts was investigated. Besides AuBr<sub>3</sub>, also AuCl<sub>3</sub>, AuCl, Johnphos-gold complex A, Ph<sub>3</sub>PAuNTf<sub>2</sub> and Ph<sub>3</sub>PAuCl were tested. A solution of 1 mM P2 and 5M NaCl was used with 2 mol% of the respective catalyst. As can be seen in Table 3, the simple gold salts AuBr<sub>3</sub> and AuCl<sub>3</sub> achieved the shortest conversion times of 2.5 and 3 h, while AuCl required 24 h (Table 3, entries 1–3). All three catalysts gave good yields while for the other gold complexes incomplete conversion of the allene was observed after 24 h (Table 3, entries 4–6).  $Ph_3PAuCl$  has to be activated with  $AgBF_4$ ; without the silver additive no reaction occurs (Table 3, entry 7). In contrast to other cases of gold catalysis in water, this indicates that no dissociation of the chloro gold complex takes place in the micellar system.<sup>[3f,i,j,11]</sup>

Under the optimized conditions (2 mol% AuBr<sub>3</sub>, 5 M NaCl, 1 mM **P2**, H<sub>2</sub>O) several  $\alpha$ -hydroxy- or aminoallenes **1** were cyclized to the corresponding heterocycles **2**, allowing a comparison of their reactivity (Scheme 1).

**Table 3.** Influence of the gold catalyst on the cycloisomeriza-tion of allene 1a in the presence of amphiphile P2.<sup>[a]</sup>

Entry	[Au]	Time [h]	Conversion [%] <sup>[b]</sup>	Yield [%]
1	AuBr <sub>3</sub>	2.5	quant.	80
1	AuCl <sub>3</sub>	3	quant.	86
3	AuCl	24	quant.	88
4	t-Bu t-Bu P-Au-NCMe	24	40	nd
5	Ph <sub>3</sub> PAuNTf <sub>2</sub>	24	29	nd
6	Ph <sub>3</sub> PAuCl <sup>[c]</sup>	24	25	nd
7	Ph <sub>3</sub> PAuCl	24	0	nd

<sup>[a]</sup> *Conditions:* 2 mol% [Au], 1 mM **P2**.

<sup>[b]</sup> Conversions were determined by GC.

<sup>[c]</sup> 2 mol% AgBF<sub>4</sub> were added.



Scheme 1. Gold-catalyzed cycloisomerization of  $\alpha$ -hydroxyand  $\alpha$ -aminoallenes 1.

Short conversion times from 0.5 to 2.5 h and good yields (80–88%) of cyclization products **2** were obtained in all cases. Particularly noteworthy is the smooth conversion of the solid, rather lipophilic allenes **1f/g** to the corresponding heterocycles; substrates of this type are unreactive in aqueous medium in the absence of an amphiphile.<sup>[5a]</sup> In general, hydroxyallenes bearing a benzyl ether (**2b–d**) or ester side chain (**2e**) react faster than their counterpart with a TBS ether (**2a**). Due to its high reactivity, we selected allene **1b** for further study of the influence of different polymers in the presence or absence of NaCl (Table 4).

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<i>t-</i> Bu.,,,,,	он ОН	DBn 2 mol% AuBr <sub>3</sub> 1 mM amphiphile 5 M NaCl H <sub>2</sub> O, r.t., 30 min	<i>t-</i> Bu'''' O OBn <b>2b</b>
Entry	Amphiphile	Conversion [%] (no NaCl) <sup>[a]</sup>	Conversion [%] (5M NaCl) <sup>[a]</sup>
1	P1	58	99
2	P2	68	99
3	P3	48	100
4	P4	35	78
5	P5	10	54
6	_	100	100 <sup>[b]</sup>

**Table 4.** Influence of the polymeric amphiphile on the goldcatalyzed cycloisomerization of allene 1b.

<sup>[a]</sup> Determined by GC.

<sup>[b]</sup> After 10 min.

A general accelerating salt effect was found for all amphiphiles - fluorinated and non-fluorinated ones. Conversions after 30 min reaction time of 10-68% in the absence of salt, and of 54-100% in the presence of 5M NaCl were observed. Moreover, the fluorinated polymers P4 and P5 showed a decreased reactivity. compared to their non-fluorinated counterparts P1-P3 (Table 4, entries 1–3 vs. 4 and 5). This trend was not influenced by the addition of salt. A rapid cyclization of allene 1b to dihydrofuran 2b was observed also in the absence of an amphiphile (Table 4, entry 6). Under these conditions, the reaction takes place in the oily layer or droplets of the allene. It must be noted however, that this procedure is not applicable to solid and/or less reactive allenes and does not allow a recycling of the catalyst.<sup>[5a]</sup>

To obtain more information about a possible correlation of micelle size and reactivity, we performed dynamic light scattering (DLS) measurements. In analogy to earlier investigations with PTS,<sup>[5a]</sup> we found a distinct increase of the micelle diameter upon addition of NaCl for all five polymers **P1–P5** (Table 5). For ex-

**Table 5.** Influence of NaCl on the micellar diameter of polymeric amphiphiles **P1-P5**.<sup>[a]</sup>

Entry	Amphiphile	Diameter without NaCl [nm]	Diameter with 5M NaCl [nm]
1 2 3 4 5	P1 P2 P3 P4 P5	$ \begin{array}{r} 14 \pm 4 \\ 10 \pm 2 \\ 23 \pm 4 \\ 41 \pm 4 \\ 7 \pm 3 \end{array} $	$\begin{array}{c} 36 \pm 3 \\ 21 \pm 4 \\ 101 \pm 22 \\ 33 \pm 5/162 \pm 11^{[b]} \\ 19 \pm 2 \end{array}$

<sup>[a]</sup> Diameter determined by DLS of a 1 mM solution of the amphiphile.

<sup>[b]</sup> Two maxima were observed.

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ample, the diameter of the micelles formed from amphiphile P3 rose from 23 nm in sweet water to 101 nm in salt water (Table 5, entry 3). However, the micelle size is not the only factor affecting the reactivity. For example, amphiphile P2 forms smaller micelles than P1 (Table 5, entry 2 vs. 1) but gives a faster cyclization of allene 1b (Table 4, entry 2 vs. 1). Likewise, the micelle diameter of **P2** with salt is similar to that of **P3** without NaCl (Table 5, entry 2 vs. 3), but their reactivity is quite different (Table 4, entry 2 vs. 3). Most striking is the low reactivity of fluorinated amphiphile P4 (Table 4, entry 4), considering the fact that this forms by far the largest micelles (Table 5, entry 4). It seems reasonable to assume that (besides the size of the micelle) the transport of substrate, catalyst, and product in and out of the micelle, as well as, the solubility of the reactants and the stabilization of the catalyst (possibly as aurate anion), affect the reactivity.

We also examined the influence of the amphiphile concentration, as well as the presence of substrate and catalyst, on the size of the micelles formed from amphiphile P2 (Table 6). The concentration of the polymer turned out to be quite important for the reactivity (cf. Table 1). Surprisingly, this does not correspond to the micelle size, which is not changing when the polymer concentration is increased from 1 to 10 mM (Table 6, entries 1 and 2). However, decreasing the concentration to 0.5 mM raises the micelle diameter from 21 to 34 nm (Table 6, entry 3). The addition of AuBr<sub>3</sub> (2 mol%) hardly affects the micelle size (Table 6, entry 4). In contrast, addition of the allene 1b causes a strong enlargement of the micelle to 74 nm (Table 6, entry 5) which does not change very much when the gold catalyst is added as well (Table 6, entry 6). TEM pictures show the presence of spherical micelles with a dark contrast caused by the loading with the gold catalyst. Altogether these data indicate a remarkable flexibility of the micellar systems which have the ability to adapt to the prevailing conditions.

In the next set of experiments we were interested how nanomicelles with a hydrocarbon or partially flu-

**Table 6.** Influence of the reaction parameters on the micellardiameter of amphiphile P2.

Entry	$c [\mathrm{mM}]^{[\mathrm{a}]}$	Addition	Diameter [nm] <sup>b)</sup>
1	1	-	$21\pm4$
2	10	-	$22\pm4$
3	0.5	_	$34\pm7$
4	1	$AuBr_3^{[c]}$	$25\pm3$
5	1	allene <b>1b</b> <sup>[d]</sup>	$74\pm22$
6	1	$AuBr_3^{[c]}$ + allene $1b^{[d]}$	$82\pm51$

<sup>[a]</sup> Concentration of amphiphile **P2** dissolved in a 5M NaCl solution.

<sup>[b]</sup> Determined by DLS.

<sup>[c]</sup> 2.3  $\mu$ mol/mL=2 mol% relative to **1b**.

[d]  $0.12 \text{ mmol mL}^{-1}$ .



 
 Table 7. Influence of the polymer on the gold-catalyzed cycloisomerization of fluorinated allene 1g.

<sup>[a]</sup> Conversion without amphiphile in 5M NaCl after 24 h: 32%.

<sup>[b]</sup> Conversions were determined by GC.

<sup>[c]</sup> Until complete conversion of allene **1g**.

orocarbon-like core affect the conversion of fluorinated substrates. Using allene 1g and the polymers P2-**P5** in the presence of 3 mol% AuBr<sub>3</sub>, we determined the conversion after 15 min, as well as the time required for full conversion (Table 7). Also for this substrate, non-fluorinated amphiphile P2 gave the best result with a reaction time of 75 min (Table 7, entry 1). Interestingly, **P4** containing a terminal  $CF_3$ group in the hydrophobic polymer segment is slightly more reactive than the non-fluorinated analogue P3 (Table 7, entry 2 vs. 3). In contrast, P5 with a longer fluorinated chain gave complete conversion only after 2 days. (Table 7, entry 4). The very low reactivity in the presence of **P5** can be explained by the polymer structure and the type of fluorocarbon chain in the micellar core. The increased size of fluorine versus hydrogen is known to be responsible for the rigid structure of fluorocarbons. Study of the dynamic nature of such fluorinated micelles by NMR spectroscopy revealed a solid-like micellar core at room temperature<sup>[8a,12a]</sup> that most likely limits substrate solubilization while micellar cores composed of hydrocarbon chains are more dynamic.<sup>[8a]</sup> Higher reaction temperature<sup>[12b]</sup> or a different polymer structure that does not favor a dense packing of the fluorocarbon chains<sup>[12c]</sup> might help to overcome the limitation of such highly fluorinated polymer amphiphiles. Without any amphiphile, the poor solubility of the substrate 1g, which is a solid, led to a very slow conversion (32% after 24 h).

The possibility of catalyst recycling is one of the main targets of sustainable chemistry. Therefore, we tested the catalyst recycling using the unpolar solvents n-hexane, isohexane or n-pentane for extraction.

**Table 8.** Recycling of the micellar catalyst solution.

<i>t-</i> Bu,,,,//	OH 1b	2 mol% AuBr <sub>3</sub> 1 mM <b>P2</b> 5 NaCl H <sub>2</sub> O, r.t.	• t-Bu'''' OBn
Run		Time <sup>[a]</sup>	Yield [%]
1		30 min	85
2		2 h	92
3		4 h	90

<sup>[a]</sup> Required for complete conversion of allene **1g**.

However, due to the formation of a foam, the extraction of the cyclization products was not feasible. Using Et<sub>2</sub>O for the extraction enables a clear phase separation, but also caused a strong loss of catalytic activity by catalyst leaching. However, when we used a mixture of *n*-pentane/Et<sub>2</sub>O (8:2, v/v) the extraction of the product 2b and recycling the micellar medium was possible (Table 8). The gradual loss of catalytic activity caused by the product extraction required an extension of the reaction time in the second and third run. In doing so, high product yields around 90% and acceptable conversion times of 2 and 4 h in the second and third run were observed (Table 8, entries 2 and 3 vs. 1). A possibility to alleviate the reactivity decrease would be the addition of more catalyst,<sup>[5c]</sup> but this was not examined here.

Finally, we also examined the possibility of performing dehydrating transformations in bulk water using the hydrophobic effect of the poly(2-oxazoline) amphiphiles. As a benchmark reaction, we selected the gold-catalyzed dehydrative cyclization of acetylenic diols to furans which has been carried previously in vitamin E-derived nanomicelles (Scheme 2).<sup>[5b]</sup> In the presence of polymer **P2** and 5M NaCl, the four diols **3a–d** were converted successfully into the corresponding furans **4a–d** with good yields of 67–82%. The reactions required 1–4 h at room temperature, except for the triphenyl-substituted diol **3c** which took 24 h to afford product **4c** with 67% yield. It should be noted



Scheme 2. Gold-catalyzed cycloisomerization of acetylenic diols 3 in the presence of polymeric amphiphile P2.

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that the presence of micelles is essential for the reaction,<sup>[5b]</sup> without the amphiphile, substrate **3a** gave only traces of furan **4a** after 2 h.

# Conclusions

We have synthesized and applied five different poly(2-oxazoline)-based amphiphiles with different compositions and hydrophobic end groups (hydrocarbon-like or partly fluorinated). The polymers were used as amphiphiles in gold-catalyzed cyclization reactions of functionalied allenes or alkynes under micellar reaction conditions. We have found a strong effect of the hydrophobic micellar core and of the salt concentration on the catalytic activity. Furthermore, detailed studies towards the correlation between micelle size and reactivity were performed. Overall, we present a new approach for fine-tuning of a catalytic system which also allows catalyst recycling. These investigations provide an important contribution to green chemistry and open the door for further studies of transition metal-catalyzed transformations in nanomicelles which will benefit from the enormous variability of amphiphilic polymers.

## **Experimental Section**

#### **Polymer Synthesis**

Pl and P2: To a solution of methyl triflate (77.18 mg, 0.471 mmol, 1.00 equiv.) in 5 mL acetonitrile was added 2methyl-2-oxazoline (1.00 g, 11.76 mmol, 25.00 equiv.). The reaction mixture was stirred at 120°C for 2 h. Subsequently, 2-heptyl-2-oxazoline (557 mg, 3.29 mmol, 7.00 equiv.) was added and the mixture was stirred at 110°C for 4 h. The polymerization was terminated by the addition of piperidine (120 mg, 1.41 mmol, 3.00 equiv.) and the mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure. The remaining residue was dissolved in chloroform and K2CO3 was added. The resulting mixture was stirred at room temperature for 4 h. The solid was removed by filtration and the polymer was precipitated with cold Et<sub>2</sub>O. After centrifugation, the polymer was dialyzed against water and lyophilized. The polymer was obtained as a white solid.

**P1:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.86$  (s, 43 H, CH<sub>3,hep</sub>), 1.28 [s, 114 H, (CH<sub>2,hep</sub>)<sub>4</sub>], 2.07–2.14 (m, 142 H), 2.96/3.05 (m, 3 H, CH<sub>3,I</sub>), 3.44 (m, 214 H, CH<sub>2</sub>CH<sub>2,backbone</sub>).

**P2:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.88$  (s, 22 H, CH<sub>3,hep</sub>), 1.30 [s, 59 H, (CH<sub>2,hep</sub>)<sub>4</sub>], 2.08–2.15 (m, 62 H), 2.96/ 3.05 (m, 3 H, CH<sub>3,I</sub>), 3.46 (m, 107 H, CH<sub>2</sub>CH<sub>2,backbone</sub>). See the Supporting information for mass spectral analysis.

**P3, P4 and P5:** To a solution of the initiators butyl triflate (for **P3**), 1-tosyloxy-4,4,4-trifluorobutane (for **P4**), or 1*H*,1*H*,2*H*,2*H*-perfluorodecyl tosylate (for **P5**; 1.00 equiv.) in 5 mL acetonitrile was added 2-heptyl-2-oxazoline (for **P3** and **P4**) or 2-methyl-2-oxazoline (for **P5**; 10.00 equiv.). The reaction mixture was stirred at 110°C for 4 h. For **P3** and **P4**, 2-methyl-2-oxazoline (1.00 g, 11.76 mmol, 25.00 equiv.) was added and the mixture stirred at 120 °C for 2 h. The polymerization was terminated by the addition of piperidine (3.00 equiv.) and the mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure. The remaining residue was dissolved in chloroform and  $K_2CO_3$  was added. The resulting mixture was stirred at room temperature for 4 h. The solid was removed by filtration and the polymer was precipitated with cold Et<sub>2</sub>O. After centrifugation, the polymer was obtained as a white solid.

**P3:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.82-0.93$  (m, 22 H, CH<sub>3,hep</sub>/CH<sub>3,I</sub>), 1.24 (s, 59 H, [CH<sub>2</sub>hep)<sub>4</sub>], 2.04–2.10 (m, 52 H), 3.18 (brs, 2 H, CH<sub>2</sub>N<sub>I</sub>), 3.41 (m, 100 H, CH<sub>2</sub>CH<sub>2,backbone</sub>).

**P4:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.85$  (s, 27 H, CH<sub>3,hep</sub>), 1.25 [s, 74 H, (CH<sub>2</sub>,hep)<sub>4</sub>], 1.82–1.90 (m, 2 H, CH<sub>2</sub>F<sub>3,1</sub>) 2.05–2.12 (m, 75 H), 3.41 (m, 132 H, CH<sub>2</sub>CH<sub>2.backbone</sub>).

**P5:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.06–2.12 (m, 42 H), 3.07 (t, 2 H, CH<sub>2</sub>N<sub>1</sub>), 3.46 (m, 57 H, CH<sub>2</sub>CH<sub>2,backbone</sub>). See the Supporting Information for mass spectral analyses.

#### Cyclization

**Standard experimental procedure:** The substrate  $(1.2 \text{ mmol mL}^{-1})$  was dissolved in a solution of the respective polymer (1 mM) in aqueous 5M NaCl. Then the gold catalyst (2 mol%) was added. The reaction was followed by TLC or GC. After complete conversion of the substrate, the mixture was filtered through Celite. To achieve good yields, thorough washing of the Celite layer with Et<sub>2</sub>O is necessary. The organic phase was dried with MgSO<sub>4</sub>, the solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography.

*tert*-Butyldimethyl[(5-(*tert*-butyl)-3-methyl-2,5-dihydrofuran-2-yl]methoxysilane (2a): 50 mg (0.176 mmol) of allene 1a, 4.5 mg of polymer P2, 438 mg NaCl, 1.5 mL H<sub>2</sub>O und 1.5 mg AuBr<sub>3</sub> were used following the general procedure. After 2.5 h complete conversion of the allene was observed. Isolation and purification on silica gel (SiO<sub>2</sub>, pentane/Et<sub>2</sub>O, 10:1) gave dihydrofuran 2a as a colorless oil; yield: 40 mg (0.14 mmol, 80%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.42 (m, 1H, CH), 4.56 (m, 1H, CH), 4.37 (m, 1H, CH), 3.68 (d, *J* = 5.3 Hz, 2H, CH<sub>2</sub>), 1.75 (s, 3H, CH<sub>3</sub>), 0.89 (s, 9H, *t*-Bu), 0.85 (s, 9H, *t*-Bu), 0.07 (s, 3H, CH<sub>3</sub>), 0.06 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  = 138.4, 122.7, 93.5, 87.8, 66.1, 34.2, 25.9, 25.8, 18.3, 13.0, -5.4, -5.4.

**2-(Benzyloxymethyl)-5-(***tert***-butyl)-3-methyl-2,5-dihydrofuran (2b):** 91 mg (0.352 mmol) of allene **1b**, 9 mg of polymer **P2**, 876 mg NaCl, 3 mL H<sub>2</sub>O und 3 mg AuBr<sub>3</sub> were used following the general procedure. After 30 min complete conversion of the allene was observed. Isolation and purification on silica gel (SiO<sub>2</sub>, pentane/Et<sub>2</sub>O, 10:1) gave dihydrofuran **2b** as a colorless oil; yield: 75 mg (0.29 mmol, 82%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.36–7.24 (m, 5H, CH<sub>Ar</sub>), 5.50 (m, 1H, CH), 4.72 (m, 1H, CH), 4.65 (dd, *J*=31.6, 12.3 Hz, 2H, CH<sub>2</sub>), 4.48 (m, 1H, CH), 3.60 (dd, *J*=10.4, 3.4 Hz, 1H, CH<sub>2</sub>), 3.53 (dd, *J*=10.5, 4.6 Hz, 1H, CH<sub>2</sub>), 1.73 (m, 3H, CH<sub>3</sub>), 0.88 (s, 9H, *t*-Bu); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  = 138.5, 137.2, 128.3, 127.7, 127.5, 123.3, 93.9, 87.5, 73.4, 71.7, 35.8, 25.5, 12.6.

#### 2-(Benzyloxymethyl)-5-butyl-3-methyl-2,5-dihydrofuran

(2c): 92 mg (0.352 mmol) of allene 1c, 9 mg of polymer P2, 876 mg NaCl, 3 mL H<sub>2</sub>O und 3 mg AuBr<sub>3</sub> were used following the general procedure. After 30 min complete conversion of the allene was observed. Isolation and purification on silica gel (SiO<sub>2</sub>, pentane/Et<sub>2</sub>O, 10:1) gave dihydrofuran 2c as a colorless oil; yield: 81 mg (0.31 mmol, 88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =7.36–7.26 (m, 5H, CH<sub>Ar</sub>), 5.50 (m, 1H, CH), 4.83 (m, 1H, CH), 4.76 (m, 1H, CH), 4.60 (dd, *J*=21.7, 12.3 Hz, 2H, CH<sub>2</sub>), 3.59 (dd, *J*=10.4, 3.4 Hz, 1H, CH<sub>2</sub>), 3.52 (dd, *J*=10.4, 4.8 Hz, 1H, CH<sub>2</sub>), 1.71 (m, 3H, CH<sub>3</sub>), 1.57–1.50 (m, 2H, CH<sub>2</sub>), 1.37–1.28 (m, 4H, CH<sub>2</sub>), 0.90 (t, *J*=6.9 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$ =138.4, 135.8, 128.3, 127.6, 127.4, 125.8, 86.8, 85.5, 73.4, 71.6, 36.1, 27.3, 22.8, 14.1, 12.6.

**2-(Benzyloxymethyl)-3-methyl-5-phenyl-2,5-dihydrofuran** (**2d**): 99 mg (0.352 mmol) of allene **1d**, 9 mg of polymer **P2**, 876 mg NaCl, 3 mL H<sub>2</sub>O und 3 mg AuBr<sub>3</sub> were used following the general procedure. After 1 h complete conversion of the allene was observed. Isolation and purification on silica gel (SiO<sub>2</sub>, pentane/Et<sub>2</sub>O, 10:1) gave of dihydrofuran **2d** as colorless oil; yield: 85 mg (0.30 mmol, 86%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.40–7.26 (m, 10H, CH<sub>Ar</sub>), 5.82 (m, 1H, CH), 5.62 (m, 1H, CH), 5.00 (m, 1H, CH), 4.66 (dd, J=11.7, 29.8 Hz, 2H, CH<sub>2</sub>), 3.71 (dd, J=3.4, 10.5 Hz, 1H, CH<sub>2</sub>), 3.64 (dd, J=4.6, 10.6 Hz, 1H, CH<sub>2</sub>), 1.80 (m, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$ =142.5, 138.4, 136.4, 128.4, 128.3, 127.6, 127.6, 127.5, 126.3, 126.0, 87.7, 87.3, 73.5, 71.4, 12.5.

[5-(*tert*-Butyl)-3-methyl-2,5-dihydrofuran-2-yl]methyl acetate (2e): 75 mg (0.352 mmol) of allene 1e, 9 mg of polymer P2, 876 mg NaCl, 3 mL H<sub>2</sub>O und 3 mg AuBr<sub>3</sub> were used following the general procedure. After 1 h complete conversion of the allene was observed. Isolation and purification on silica gel (SiO<sub>2</sub>, pentane/Et<sub>2</sub>O, 10:1) gave dihydrofuran 2e as a colorless oil; yield: 60 mg (0.28 mmol, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =5.50 (m, 1 H, CH), 4.73 (m, 1H, CH), 4.44 (m, 1H, CH), 4.19 (dd, *J*=11.8, 2.9 Hz, 1H, CH<sub>2</sub>), 4.07 (dd, *J*=11.8, 5.0 Hz, 1H, CH<sub>2</sub>), 2.05 (d, *J*= 0.7 Hz, 3H, CH<sub>3</sub>), 1.72 (m, 3H, CH<sub>3</sub>), 0.85 (s, 9H, *t*-Bu); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$ =171.1, 135.8, 124.2, 94.1, 86.0, 65.4, 35.7, 25.5, 20.9, 12.4.

2-(Benzyloxymethyl)-5-butyl-3-methyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (2f): 144 mg (0.352 mmol) of allene 1f, 9 mg of polymer P2, 876 mg NaCl, 3 mL H<sub>2</sub>O und 3 mg AuBr<sub>3</sub> were used following the general procedure. After 2 h complete conversion of the allene was observed. Isolation and purification on silica gel (SiO<sub>2</sub>, pentane/Et<sub>2</sub>O, 10:1) gave dihydro-1*H*-pyrrole **2f** as a colorless oil; yield: 120 mg (0.29 mmol, 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.75$  (d,  $J = 8.3 \text{ Hz}, 2 \text{ H}, \text{ CH}_{\text{Ar}}), 7.32-7.24 \text{ (m, 3H, CH}_{\text{Ar}}), 7.22-7.14$ (m, 4H, CH<sub>Ar</sub>), 5.40 (m, 1H, CH), 4.57 (m, 1H, CH), 4.46 (m, 1H, CH), 4.33 (d, J = 12.2 Hz, 1H, CH<sub>2</sub>), 4.18 (d, J =12.2 Hz, 1 H, CH<sub>2</sub>), 4.00 (dd, J=10.5, 3.2 Hz, 1 H, CH<sub>2</sub>), 3.68  $(dd, J = 10.5, 1.9 Hz, 1H, CH_2), 2.34 (s, 3H, CH_3), 1.98-1.90$ (m, 1H, CH<sub>2</sub>), 1.76–1.68 (m, 1H, CH<sub>2</sub>), 1.67 (s, 3H, CH<sub>3</sub>), 1.30–1.10 (m, 4H, CH<sub>2</sub>), 0.85 (t, J = 7.2 Hz, 3 H CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 142.4$ , 139.4, 138.1, 134.9, 129.1, 128.1, 127.3, 127.3, 126.7, 124.8, 72.6, 69.9, 67.9, 67.2, 34.1, 26.5, 22.6, 21.3, 14.0, 13.6.

**2-[3,5-Bis(trifluormethyl)phenyl]-4-methyl-2,5-dihydrofuran (2g):** 104 mg (0.352 mmol) of allene **1g**, 9 mg of polymer **P2**, 876 mg NaCl, 3 mL H<sub>2</sub>O und 3 mg AuBr<sub>3</sub> were used following the general procedure. After 2.5 h complete conversion of the allene was observed. Isolation and purification on silica gel (SiO<sub>2</sub>, pentane/Et<sub>2</sub>O, 10:1) gave dihydrofuran **2g** as a colorless oil; yield: 83 mg (0.28 mmol, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.78 (s, 1H, CH<sub>Ar</sub>), 7.74 (s, 2H, CH<sub>Ar</sub>), 5.86 (m, 1H, CH), 5.51 (m, 1H, CH), 4.79–4.73 (m, 1H, CH<sub>2</sub>), 4.69–4.64 (m, 1H, CH<sub>2</sub>), 1.85 (m, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 145.5, 138.2, 131.7 (q,  $J_{CF}$ =33.3 Hz), 126.4 (m), 123.7 (q,  $J_{CF}$ =272.7 Hz), 122.7, 121.5 (m), 86.2, 78.8, 12.2.

**5-Butyl-2,3-dimethylfuran (4a):** 60 mg (0.352 mmol) of diol **3a**, 9 mg of polymer **P2**, 876 mg NaCl, 3 mL H<sub>2</sub>O und 3 mg AuBr<sub>3</sub> were used following the general procedure. After 2 h complete conversion of the diol was observed. Isolation and purification on silica gel (SiO<sub>2</sub>, pentane/Et<sub>2</sub>O, 10:1) gave furan **4a** as a colorless oil; yield: 45 mg (0.28 mmol, 80%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$ =5.75 (s, 1H, CH<sub>Ar</sub>), 2.53 (t, *J*=7.6 Hz, 2H, CH<sub>2</sub>), 2.16 (s, 3H, CH<sub>3</sub>), 1.90 (s, 3H, CH<sub>3</sub>), 1.61–1.50 (m, 2H, CH<sub>2</sub>), 1.40–1.35 (m, 2H, CH<sub>2</sub>), 0.93 (t, *J*=7.4 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta$ =153.5, 145.1, 114.1, 107.7, 30.4, 27.7, 22.3, 13.8, 11.2, 9.9.

**2,3-Dimethyl-5-phenylfuran (4b):** 67 mg (0.352 mmol) of diol **3b**, 9 mg of polymer **P2**, 876 mg NaCl, 3 mL H<sub>2</sub>O und 3 mg AuBr<sub>3</sub> were used following the general procedure. After 1 h complete conversion of the diol was observed. Isolation and purification on silica gel (SiO<sub>2</sub>, pentane/Et<sub>2</sub>O, 10:1) gave furan **4b** as a colorless oil; yield: 48 mg (0.28 mmol, 80%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =7.62 (d, J=8.3 Hz, 2H, CH<sub>Ar</sub>), 7.36 (t, J=7.6 Hz, 2H, CH<sub>Ar</sub>), 7.21 (t, J=7.4 Hz, 1H, CH<sub>Ar</sub>), 6.46 (s, 1H, CH<sub>Ar</sub>), 2.30 (s, 3H, CH<sub>3</sub>), 2.00 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$ =150.9, 147.3, 131.2, 128.5, 126.5, 123.1, 116.1, 108.3, 34.1, 22.4.

**2,3,5-Triphenylfuran (4c):** 111 mg (0.352 mmol) of diol **3c**, 9 mg of polymer **P2**, 876 mg NaCl, 3 mL H<sub>2</sub>O und 3 mg AuBr<sub>3</sub> were used following the general procedure. The reaction was stopped after 24 h. Isolation and purification on silica gel (SiO<sub>2</sub>, pentane/Et<sub>2</sub>O, 10:1) gave furan **4c** as white solid; yield: 70 mg (0.24 mmol, 67%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.83–7.79 (m, 2H, CH<sub>Ar</sub>), 7.69–7.65 (m, 2H, CH<sub>Ar</sub>), 7.54–7.50 (m, 2H, CH<sub>Ar</sub>), 7.48–7.41 (m, 4H, CH<sub>Ar</sub>), 7.40–7.28 (m, 5H, CH<sub>Ar</sub>), 6.86 (m, 1H, CH<sub>Ar</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 152.5, 147.9, 134.3, 131.1, 130.5, 128.7, 128.7, 128.6, 128.4, 127.5, 127.5, 127.3, 126.1, 124.5, 123.8, 109.4.

**2,3-Diphenylfuran (4d):** 84 mg (0.352 mmol) of diol **3d**, 9 mg of polymer **P2**, 876 mg NaCl, 3 mL H<sub>2</sub>O und 3 mg AuBr<sub>3</sub> were used following the general procedure. After 4 h complete conversion of the diol was observed. Isolation and purification on silica gel (SiO<sub>2</sub>, pentane/Et<sub>2</sub>O, 10:1) gave furan **4d** as a white solid; yield: 64 mg (0.29 mmol, 82%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =7.46 (m, 2H, CH<sub>Ar</sub>), 7.43 (m, 1H, CH<sub>Ar</sub>),7.36–7.33 (m, 2H, CH<sub>Ar</sub>), 7.31–7.27 (m, 2H, CH<sub>Ar</sub>), 7.23–7.19 (m, 3H, CH<sub>Ar</sub>), 7.18–7.16 (m, 1H, CH<sub>Ar</sub>), 7.48 (m, 1H, CH<sub>Ar</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$ =148.6, 141.5, 134,4, 131.2, 128.7, 128.6, 128.4, 127.5, 127.1, 126.3, 122.3, 114.0.

**Recycling:** The reaction was performed as described above with 0.352 mmol of allene **1b** in 2 mL polymer solution (1 mM **P2**, 5M NaCl, 2 mL H<sub>2</sub>O). After complete conversion, the product was extracted with a mixture of *n*-pen-

tane/Et<sub>2</sub>O (8:2, v/v). This was accomplished by adding a portion of the solvent mixture, stirring of the entire reaction mixture for 5–10 min, and removal of the organic layer with a pipette. This procedure was repeated until no more than traces of the product remained in the micellar phase (detection by TLC). The combined organic phases were dried with MgSO<sub>4</sub>, the solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography. The micellar catalyst solution was exposed to reduced pressure to remove traces of the organic solvent. Then it was reused by addition of another portion of the substrate.

## Acknowledgements

We thank Prof. Dr. Jörg Tiller (TU Dortmund) for providing the devices for DLS and fluorescence measurements. We also thank Monika Meuris (Group Prof. Jörg Tiller) for the TEM measurements. Financial support by SusChemSys (which is co-financed by the Regional Development Fund (Investing in Your Future) of the European Union and the state of North Rhine-Westphalia), the European Metrology Research Programme (EMRP, project IND15 SurfChem) and the Adolf-Martens-Fund is gratefully acknowledged. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

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