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Amphiphilic Poly(oxazoline)s – Synthesis and Application for Micellar Catalysis

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Introduction

Homogeneous and heterogeneous catalytic processes compete on industrial scale for more then three decades [1]. The advantages of homogeneous catalysis are beside others high activity, mild reaction conditions, high selectivity and no diffusion problems. The disadvantages of such systems include difficulties with recycling of the catalyst and product separation [2].

Table 1: Characteristics of homogenous versus heterogenous catalysis.

	homogeneous catalysis	**heterogenous catalysis**
activity (with respect to metal content)	high	variable, only on surface
reaction conditions	mild	harsh
catalyst life time	variable	long
catalyst recycling	expensive	not necessary
mechanistic understanding	In situ spectroscopy	seldom
selectivity	high	variable
diffusion problems	no	possible

Possibilities to combine the benefits of both homogeneous and heterogeneous catalysis are liquid-liquid two phase systems [3] but also micro heterogenization via colloidal assemblies [4].

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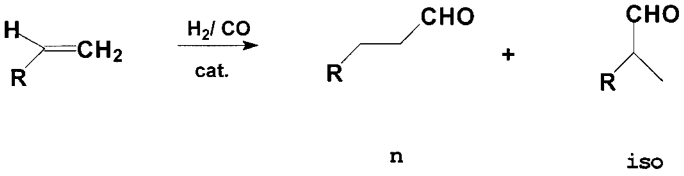
Aqueous biphasic catalysis represents the most important special case of liquid-liquid biphasic processes and has revolutionized the catalytic process methodology allowing the separation of reaction products from the homogenous catalyst phase by simple phase separation (decantation) after the reaction is complete to recycle the catalyst [5]. Due to the physiological, economical and the safety related process engineering in combination with chemical and physical properties of water, aqueous biphasic catalytic processes gained enormous importance over the last 15 years in many industrial processes. Some examples are summarized in the following Table 2.

Table 2: Industrial processes of two-phase catalysis with water as one phase.

process/products	catalyst	capacity (t/a)	company
Hydrodimerisation butadiene → octadienol	Ru/TPPTS	5000	Kuraray
selective hydrogenation → unsaturated alcohols	Ru/TPPTS	----	Rhone-Poulonc
C-C coupling → geranylacetone	Ru/TPPTS	> 1000	Rhone-Poulonc
hydroformylation → butanal, pentanal	Ru/TPPTS	> 300000	Hoechst AG Union Carbide
SHOP → C_{12}-C_{20} α-olefines	Ni/div.	> 10^6	Shell

Hydroformylation is a major industrial process producing aldehydes from olefins, carbon monoxide and hydrogen in the presence of a rhodium catalyst combined with phosphorous ligands.



Scheme 1

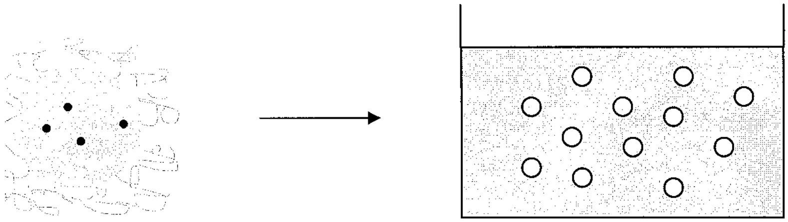
The industrial process of the hydroformylation was developed by the Ruhr-Chemie AG [6] using the highly water-soluble catalyst RhH(CO)(tppts)$_3$ in a two-phase system. Although short chain olefins could be successfully converted to their corresponding aldehydes [7], the catalyst showed low activity in the hydroformylation of higher olefins, such as 1-octen. The major reason for that is the limited mass transfer as a result of low water solubility of such long alkyl derivatives in water [8].

Several approaches have been used to improve the reaction rate including surfactants [9], stablilization of the catalytic groups at the liquid-liquid interface with promoter ligands [10] and supported aqueous phase catalysts [11]. Problems with product isolation and catalyst recycling, however, limit the scope of these approaches.

Our approach to solve the problem of limited mass transfer of hydrophobic reactants is the use of block copolymer forming micelles. It's well recognized in all branches of chemistry that the role of a chemical reaction can be very sensitive to the nature of the reactant environment. The presence of micellar aggregates can provide therefore a beneficial effect through the potential to solubilize a reactant that would otherwise not have significant solubility in the reaction media. To prepare a catalytically active micelles for the hydroformylation process of long chain olefins, the catalyst has to be part of the hydrophobic core, as well.

Micelles, microscopically dispersed in the homogenous aqueous phase, that are able to solubilize both, the hydrophobic reactant and the catalyst represent therefore a promising system for homogenous two-phase catalysis.

Idea of the catalytically active micelle
- hydrophobic core replaces one solvent phase
- solubilization of unpolar substrates
- fixation of catalyst



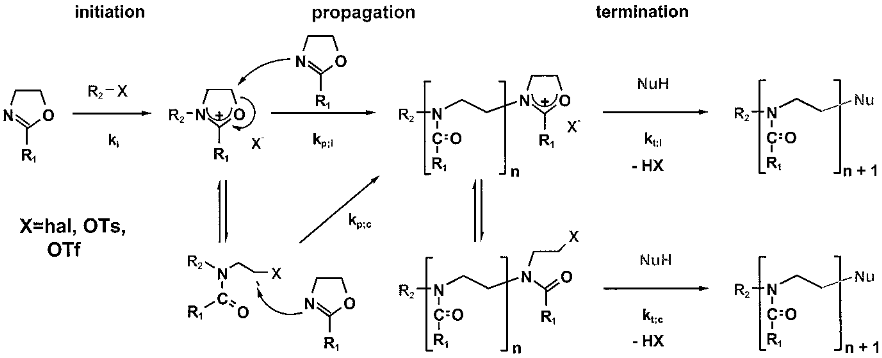
Scheme 2: Micellar catalysis as a approach for homogenous two-phase catalysis

In this presentation, micellar catalysis is applied to the hydroformylation of 1-octene:

Synthesis of amphiphilic block copolymers

Choice of monomer system

The cationic ring-opening polymerisation of 2-oxazolines provides among many others an excellent methodology for the design of amphiphilic block- and graft copolymers [12] and the easy introduction of functional end-groups via controlled initiation or termination [13]. In addition the synthetic versatility of the 2-oxazoline monomer system offers the possibility to control the polarity of the resulting polymer from hydrophilic to lipophilic and fluorophilic.

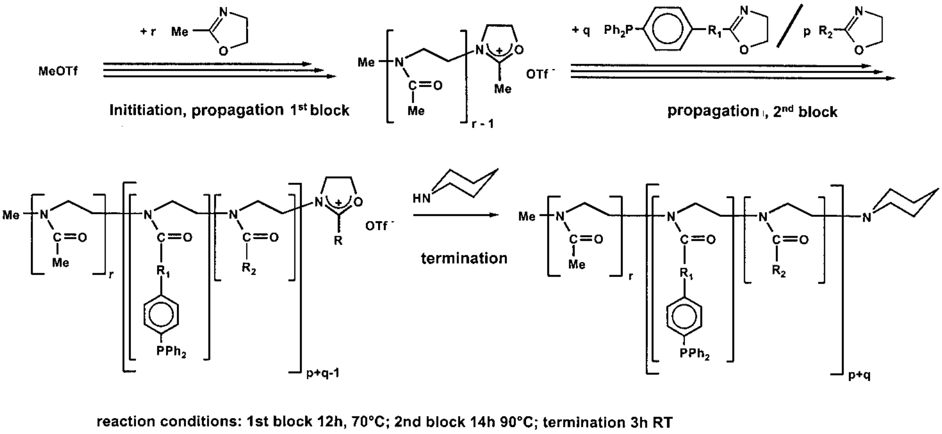


Scheme 3: Mechanism of 2-oxazoline polymerization

The introduction of suitable ligands which are able to immobilize attractive transition metals, e.g. Rh for the hydroformulation is a critical step for the preparation of a micellar catalyst.

An amphiphilic polyoxazoline with triphenylphosphine moieties could become available, i) via sequential monomer addition techniques of suitable monomers, ii) by introducing the desired functional group with the terminating agent or iii) via controlled initiation, using initiators with carry triphenylphosphine units.

We chose the first route, since it offered the best control over metal ligand concentration in the miceller system. The synthesis of the oxazoline monomer with a triphenyl side chain and it's subsequent incorporation in amphiphilic blockcopolymers is depicted in scheme 4.



Scheme 4: Synthesis of amphiphilic block copolymers by sequential monomer addition

It turned out, however, that the triphenylphosphine units are not inert under conditions which are necessary for the ring-opening polymerization of the oxazoline. Model studies indicated almost complete alkylation oft the triphenylphosphine side chains by the growing cationic chain end, see figure 1.

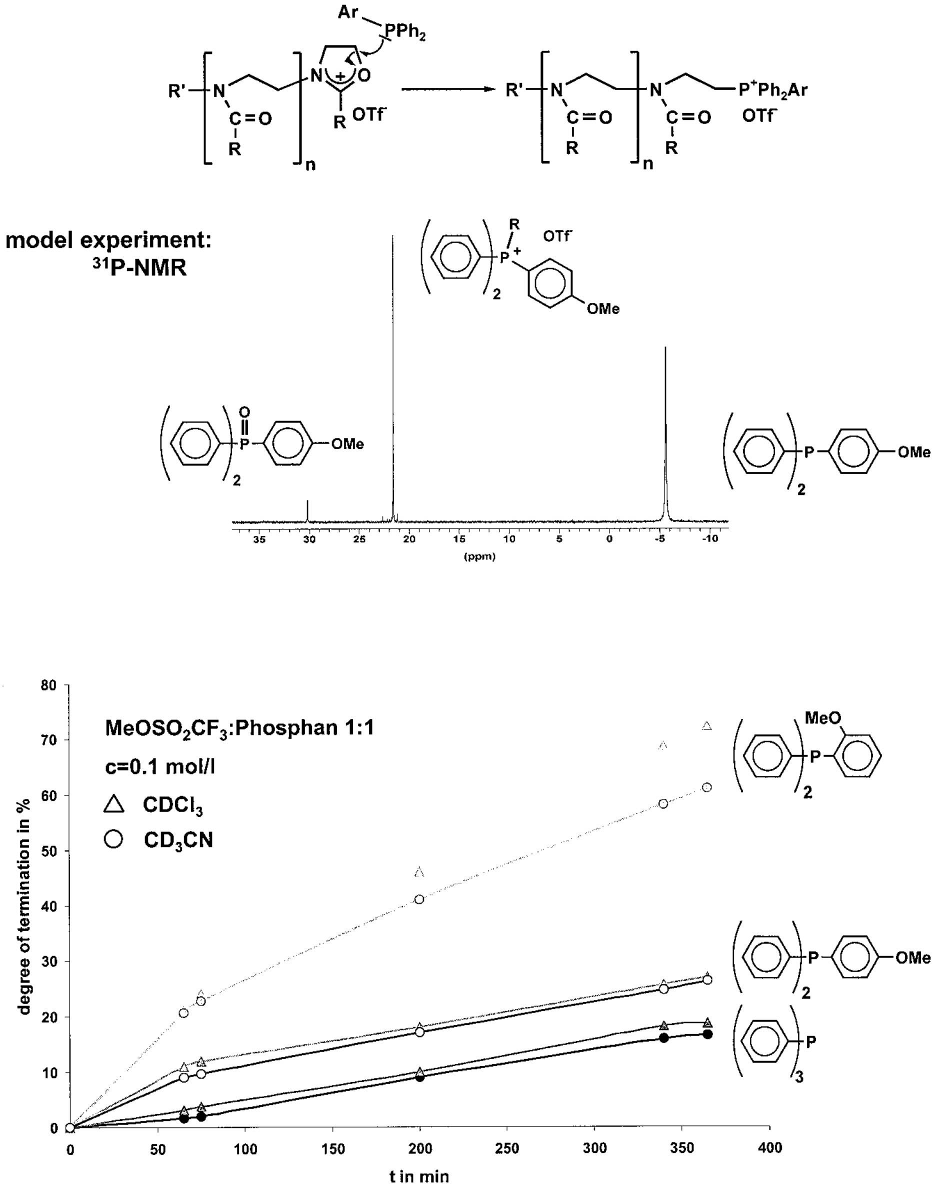


Figure 1: Study of the termination reaction of methyltriflate with different phosphane derivatives

Functionalization of a polymer precursor

A possibility to overcome the problem is the post-analogues incorporation of the triphenylphosphine units using Pd catalysed P-C coupling of diarylphosphine units with aryliodide polymer side chains.

Model studies showed, that the palladacyclus developed by Herrmann et al. [14] showed high activity and selectivity

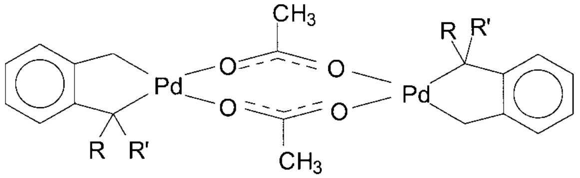


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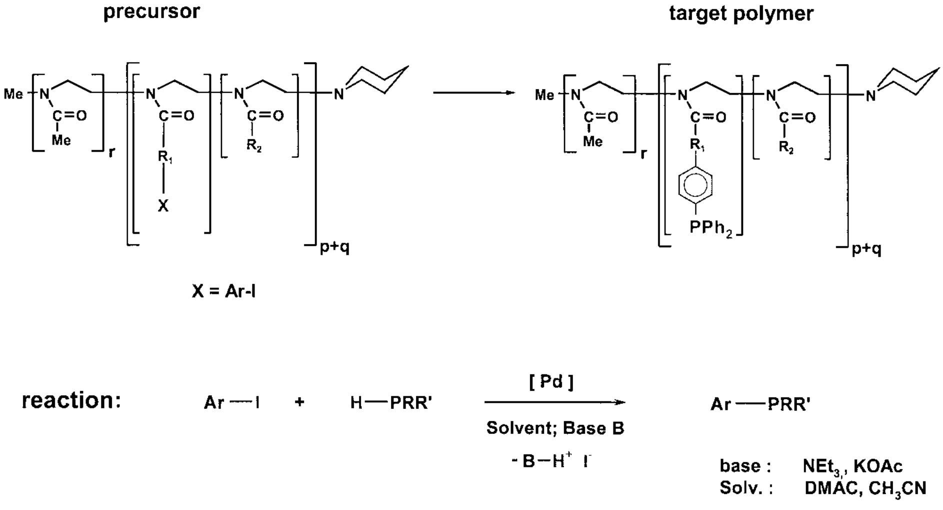
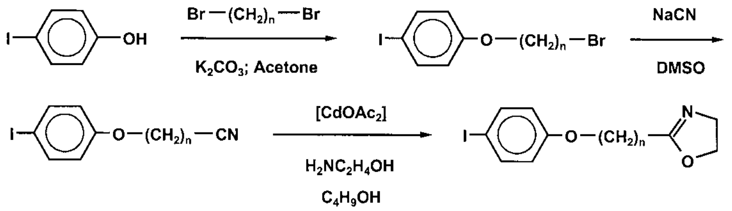
Figure 2: Palladacyclus by Herrmann et *al.*



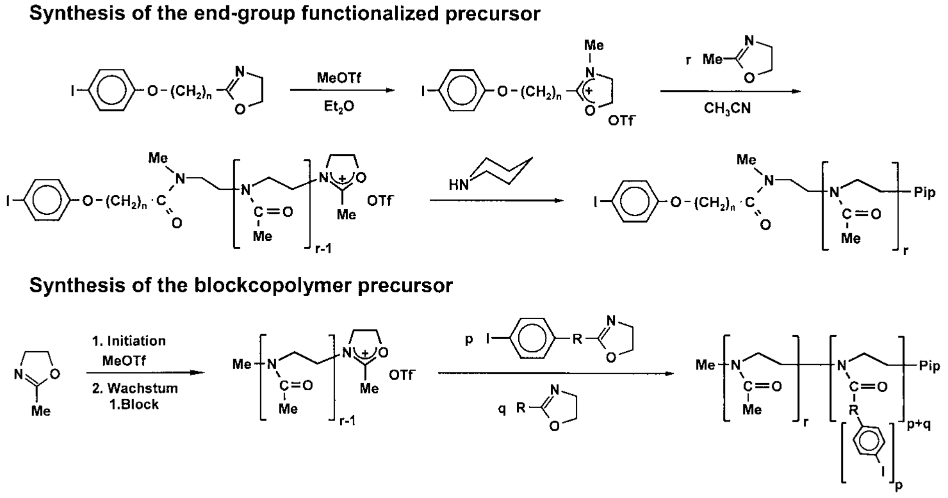
Scheme 5: Precursor route for the synthesis of functionalised amphiphilic polymers

At least three different routes were developed for the synthesis of aryliodine substituted 2-oxazolines. The pathway depicted in scheme 6 was found to be most suitable and was preferred in the following studies:



Scheme 6: Synthesis of the aryliodide containing oxazoline monomer

The complete scheme for the synthesis of the precursor polymer is shown in the following scheme 7. First, 2-Methyl-2-oxazoline is initiated with MeOTf – the length of the resulting water-soluble poly(2-methyl-2-oxazoline) was controlled by the ratio of [M] : [I]. After the complete conversion of the first monomer a mixture of the aryliodine derivative and an alkyl substituted oxazoline was added and copolymerized. Finally, the growing chains were terminated by the addition of piperidine.



Scheme 7: Complete scheme of the precursor polymer synthesis

The polymer modification gave the desired polymers in almost quantitative yield.

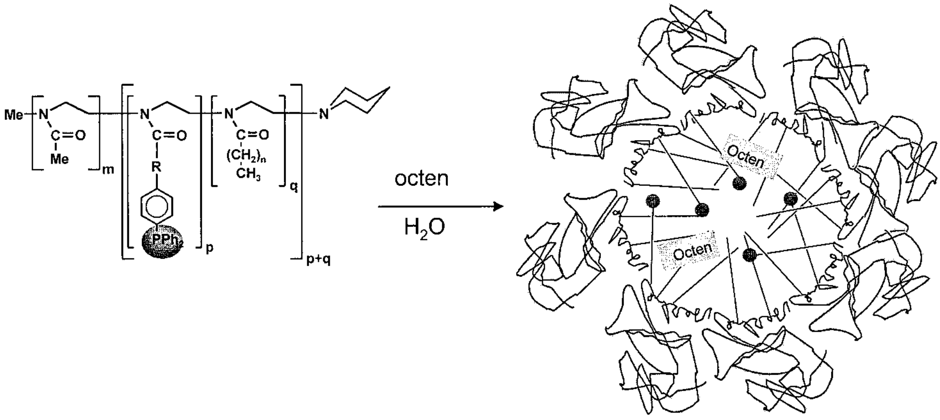
Table 3: Results of the polymer modification by post-analogue Pd-catalysis.

Solv.	**[Pd]**	ε	τ	**t in h**	**c in %**	**remarks**
CH_3CN	$Pd(OAc)_2$	100	2,5	14	85	side products
DMAc	$Pd(OAc)_2$	100	2,5	14	90	side products
CH_3CN	1	50	2,5	14	>95	----
CH_3CN	1	100	2,5	10	>95	----
CH_3CN	1	250	1,2	48	>95	----

$\varepsilon = n(Ar\text{-}I):n(Pd)$; $\tau = n(HPPh_2):n(Ar\text{-}I)$

Hydroformylation of 1-octene

As already mentioned, for an industrial application of the two phase catalysis towards hydroformylation it is essential that the educt (olefine) is reasonable good soluble in water. Therefore, usually higher olefins can not be converted into the corresponding aldehydes by a common two phase hydroformylation process due to their poor solubility in water. The strategy of this work is shown in the following scheme using micelle formation of amphiphilic blockcopolymers with triphenylphosphine ligands covalently linked to the hydrophobic part of the polymer backbone.



Scheme 7: Micelle formation of amphiphilic blockcopolymers

Above the critical micelle concentration, the amphiphilic blockcopolymers start to form micelles, which have a hydrophobic core where the phosphine ligands and consequently the transition metals are immobilized and a hydrophilic shell to guarantee water-solubility. Since

1-octene is good soluble in the micellar core, its local concentration close to the catalytic center is high, which is essential for its efficient hydroformylation.

The following table summarizes experimental data for the hydroformylation of 1-octene under different experimental conditions. The results in the presence of TPPTS (run 1), SDS/TPPTS (run 2) and SDS/PPh_3) (run 3) indicate low catalytic activity with almost no product formation and TON values ranging from 20-100 and TOF values between 2 and 10.

The catalytic results improve dramatically in the presence of the prepared polymeric macro ligands. Product yield increases up to 81 % with TON and TOF values of up to 4650 and 1610, respectively.

Table 4: First results of the hydroformylation in the presence different catalyst systems.

run	catalyst	P:Rh	Oc:Rh	t in h	yield	c in %	n/iso	TON	TOF
1	TPPTS	25	2000	10	<1%	<5	73:27	20	2
2	SDS, TPPTS	25	2100	10	<1%	<6	72:28	64	6
3	SDS, PPh_3	25	2000	10	<1%	<8	73:27	100	10
4	$Me_{30}IPP7_4Hep_2$	29	2000	14	24%	99	80:20	480	34
5	$Me_{30}IPP7_2Hep_4$	22	7400	4	81%	95	76:24	4650	1610

c(Phos.) = $1.0 * 10^{-3}$ for run **1**, **2**, **3**, **5** and $2.5 * 10^{-3}$ for run **4**; standard: IO

Summary

Novel amphiphilic blockcopolymers for micellar catalysis applications were prepared by living cationic polymerisation of 2-oxazoline monomers. Phosphine ligands suitable for transition metal immobilization were introduced by palldium catalyzed post analogue P-C coupling of aryliodide containing polymers with bisaryl phosphine.

First results of the 1-octene hydroformylation indicate high catalytic activity of the micellar catalyst. This supports our idea that this system functions as a nanoreactor and should allow us to extend this strategy also to other catalytic processes.

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