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Triphenylphosphane-Functionalised Amphiphilic Copolymers: Tailor-Made Support Materials for the Efficient and Selective Aqueous Two-Phase Hydroformylation of 1-Octene

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Abstract: Amphiphilic copolymers (random **P1** and block **P2**) based on 2-oxazolines were synthesised with triphenylphosphane ligands covalently linked to the polymers by means of a metal-free synthesis route. The resulting macroligands were used in the aqueous two-phase hydroformylation of 1-octene. The influence of the polymer architecture (random and block copolymers) on activity and selectivity of the hydroformylation reaction was investigated and compared with that of nonfunctionalised copolymers (random **P3** and block **P4**) and Rh^I/triphenylphosphane trisulfonate as a water-soluble catalyst. The highest activities were observed for the random copolymer **P1** ($p = 50$ bar, $T = 100\,°C$, $c = 8 \times 10^{-4}\,mol\,L^{-1}$) with a turnover frequency (TOF) of $3700\,h^{-1}$, whereas the corresponding block copolymer **P2** reached TOF numbers of $1630\,h^{-1}$. Additionally, both macroligands indicated efficient suppression of isomerisation and led to almost constant *n*/iso selectivities of about 3 after complete substrate conversion. Copolymers **P3** and **P4** showed, under identical reaction conditions, strong isomerisation after 40–60% conversion (*n*/iso $\approx$ 0.7) and maximum activities of $1560\,h^{-1}$ (**P3**) and $1330\,h^{-1}$ (**P4**) at a concentration of $5 \times 10^{-3}\,mol\,L^{-1}$.

Keywords: amphiphiles · hydroformylation · immobilization · polymers · supported catalysts

Introduction

Hydroformylation of terminal olefins is one of the most important homogeneously catalysed reactions in industry for the large-scale production of aldehydes. Aqueous two-phase catalysis of lower olefins by using the Ruhrchemie/Rhône–Poulenc process has revolutionised this reaction by using an environmentally benign reaction medium with the option of catalyst recycling.[1,2] In the case of higher olefins, however, the hydroformylation reactions are limited by the solubility of the substrate in the aqueous phase.

Over the past decades many approaches have been exploited to overcome this limitation and accelerate mass-transfer processes by increasing either the mutual solubility of the components or the mobility across the aqueous–organic phase boundaries. The employment of cosolvents, such as methanol, ethanol, or propanol;[3] the use of supported aqueous-phase catalysts (SAPC)[4] or additives such as surfactants;[5] modified cyclodextrin derivatives;[6] amphiphilic phosphane ligands with surfactant structures[7] and various polymer-supported catalysts[8] have been reported with this in mind. Other strategies to overcome the mutual immiscibility of the catalyst and the substrate include the use of so-called “smart” ligands, which display inverse temperature behaviour in water and transport the catalyst at higher temperature in the organic phase and move it back to the aqueous phase at lower temperatures,[9] fluorous/organic biphasic mixtures[10] or the application of supercritical CO_2 as solvent[11] in the hydroformylation.

The reasons for the still somewhat lower activities compared with homogeneous hydroformylation are twofold. In the case of amphiphilic additives such as surfactants, the water-soluble $[Rh(CO)H(TPPTS)_3]$ catalysts (TPPTS = triphenylphosphane trisulfonate) as well as the substrate are, at first glance, both in the aqueous phase. On a microscopic level, however, the hydrophobic substrate presumably stays

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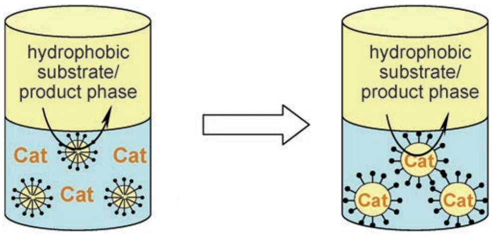
in the hydrophobic domains of the micellar aggregates while the catalyst is homogeneously dissolved in the aqueous phase and thus phase-separated from the substrate. On the other hand, the use of smart ligands, organic/fluorous solvent mixtures or supercritical CO$_2$, provide nearly homogeneous reaction conditions during hydroformylation. However, the high surface area and the resulting micellar effect, which account for the good activities when using amphiphiles, are gone. The question remains how to combine the advantages of both approaches: forcing the catalyst and the substrate into the same hydrophobic domain on the one hand, while taking advantage of the micellar effect, that is, compartmentalisation and concentrating reactants, thereby altering the chemical rate of the reaction, on the other hand. In recent years our work has focussed on the synthesis of various amphiphilic block copolymers functionalised with metal catalysts. Beyond simple catalyst immobilisation on a polymer, these soluble macroligands form micellar aggregates in water and consequently act as nanoreactors for the efficient conversion of hydrophobic substrates in aqueous media.[12] In the case of aqueous two-phase catalysis, this approach becomes particularly attractive. Here the micellar environment forces the substrate and catalyst into the same micellar core phase, and due to the insolubility of the polymer in the 1-octene substrate, the polymer-supported catalyst should remain in the aqueous phase under hydroformylation conditions (see Scheme 1). Here we describe the preparation of two amphiphilic copolymers (random and AB block copolymers) with triphenylphosphane (TPP) units covalently attached to the polymer backbone. The two copolymers were studied for the aqueous two-phase hydroformylation of 1-octene and the results were compared with the results from two nonfunctionalised copolymers, which were used as polymeric amphiphiles in the presence of the well-known Rh^{I}/TPPTS system as a water-soluble catalyst.



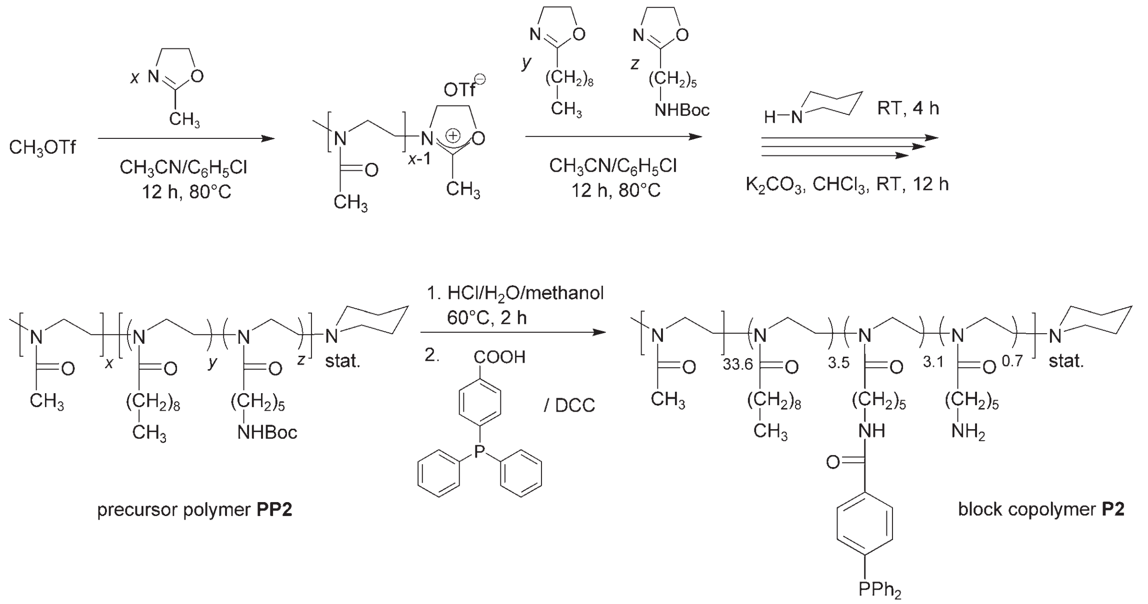
Scheme 1. Left: Current situation of water-soluble catalysts phase-separated from the hydrophobic substrate dissolved in the micellar phase. Right: Our approach of amphiphilic macroligands that form micelles with the catalyst, and the substrate during the reaction, in the hydrophobic core.

Results and Discussion

Synthesis of amphiphilic, TPP-functionalised copolymers: Several water-soluble polymers have already been investigated as carriers for phosphane ligands and tested in the hydroformylation of longer-chain alkenes. However, little is known about the effect of different copolymer compositions on activity and selectivity in the hydroformylation reaction. The cationic ring-opening polymerisation of 2-oxazolines provides an excellent methodology for the preparation of different polymer compositions, including random copolymers and block copolymers.[13]

Recently, Persigehl et al. reported on the synthesis of TPP-functionalised amphiphilic block copolymers for catalysis application.[14] The TPP unit was introduced into the polymer by means of the polymer-analogous coupling of diphenylphosphane to the iodoaryl-containing polymer precursor in the presence of a Pd catalyst. Although the coupling reaction proceeded quantitatively, it turned out that the residual Pd catalyst was extremely difficult to remove and effected hydroformylation activities dramatically due to the very low amounts of rhodium employed therein. Consequently, we decided to develop a metal-free route to TPP-functionalised copolymers. The introduction of the triphenylphosphane moieties to the amphiphilic copolymers was achieved by using a polymer-analogous amide coupling of 4-diphenylphosphanobenzoic acid and a poly(2-oxazoline) with pendent primary amine groups (Scheme 2). The *tert*-butoxycarbonyl (Boc)-protected amine-functionalised monomer 2-[5-(amino-*tert*-butoxycarbonyl)pentyl]-2-oxazoline (BocOx) was synthesised according to a literature procedure.[15] In the next step, a random copolymer (**PP1**) and a block copolymer (**PP2**) consisting of 2-methyl-2-oxazoline (MeOx), 2-nonyl-2-oxazoline (NonOx) and BocOx were synthesised by using living cationic polymerisation. The random copolymer **PP1** was synthesised by using simple copolymerisation of the three monomers. In the case of **PP2**, sequential polymerisation of 2-methyl-2-oxazoline was used to form the hydrophilic block, followed by the polymerisation of a mixture of NonOx and BocOx to give the hydrophobic block (see also Scheme 2). Methyl triflate (CH$_3$OTf) was used as the initiator and piperidine as the highly efficient termination agent.[16]

The NonOx monomer is necessary to increase the hydrophobicity of copolymers **P1** and **P2**. The chosen ratio of MeOx/NonOx/BocOx was 30:4:4. The copolymers show narrow polydispersity indexes (PDIs) of 1.15 (**PP1**) and 1.09 (**PP2**), indicative of a living polymerisation mechanism. After the polymerisation of the precursor polymers **PP1** and **PP2** was complete, free primary amine groups were obtained after deprotection in methanolic hydrochloric acid. The success of the deprotection reaction to give **PP1–NH$_2$** and **PP2–NH$_2$** can be followed by observing the disappearance of the ^{1}H NMR signals of the CH$_3$–Boc group at $\delta = 1.38$ and 1.36 ppm. Triphenylphosphane groups were linked to the polymer by amide bonds because of their high stability, especially towards hydrolysis, which is important for any catalytic reactions carried out in water. Therefore, an excess of 4-diphenylphosphanobenzoic acid (1.5 equiv per amine function) was reacted with the amino-deprotected **PP1–NH$_2$** and **PP2–NH$_2$** by using dicyclohexylcarbodiimide (DCC) as



Scheme 2. Synthesis of the precursor polymer **PP2** with Boc-protected amine functionalities and its subsequent conversion to the triphenylphosphane-functionalised amphiphilic block copolymer **P2** (stat. = statistical/random).

the coupling reagent (Scheme 2). The success of the reaction was monitored through changes in the ^1H (Figure 1) and ^{31}P NMR spectra.

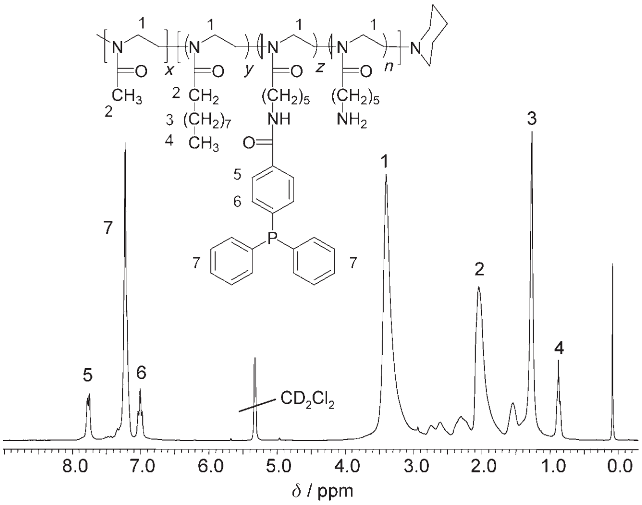


Figure 1. ^1H NMR spectrum of **P2** (CD_2Cl_2, 300.13 MHz, $T = 20$ °C).

The amount of triphenylphosphane moieties that were successfully linked to the polymer was calculated by using ^1H NMR spectroscopy to be 100 % for **P1** and 81 % for **P2**. Successful coupling of the TPP ligand to the copolymers was confirmed by using ^{31}P NMR spectroscopy showing one signal at $\delta = 4.81$ (**P1**) and 4.77 ppm (**P2**), which can be ascribed to the polymer-bound 4-diphenylphosphanobenzoic acid. Unreacted 4-diphenylphosphanobenzoic acid at $\delta = -4.60$ ppm, as well as the corresponding phosphane oxide as possible byproduct at $\delta = 22.7$ ppm, were not observed and supported our ^1H NMR observations.

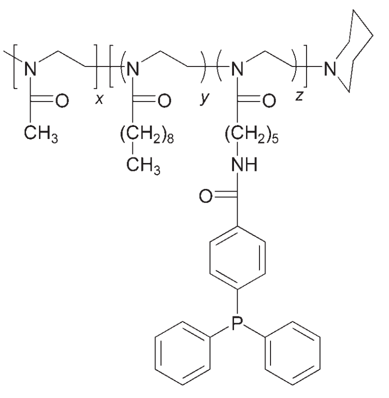
The random **P3** and block **P4** copolymers based on 2-methyl-2-oxazoline and 2-nonyl-2-oxazoline were prepared as references. The ratio chosen for the hydrophilic (MeOx) to the hydrophobic (NonOx) monomers was 30:6 to provide good water solubility of the polymers while still retaining an amphiphilic character. The resulting copolymers show very narrow PDIs of 1.03 for both polymers **P3** and **P4**. The molar masses and copolymer compositions were calculated from ^1H NMR spectra and are summarised in Table 1

Table 1. Analytical data of the copolymers **PP1**–**P4**.

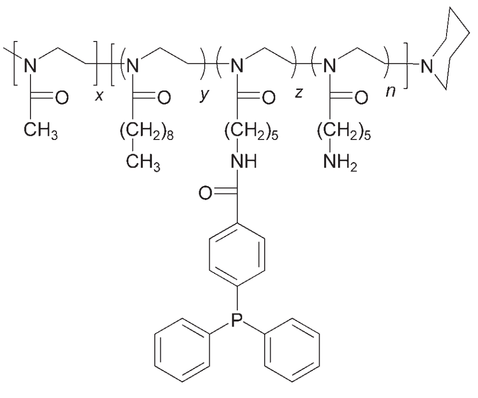
Polymer	Composition (^1H NMR)	M_n [g mol^{-1}][a]	M_w/M_n[b]
PP1	$MeOx_{34.9}NonOx_{4.6}BocOx_{4.4}$	5100	1.15
PP2	$MeOx_{33.6}NonOx_{3.5}BocOx_{3.8}$	4620	1.09
P1	$MeOx_{34.9}NonOx_{4.6}TPP\text{-}Ox_{4.4}$	5540	1.08
P2	$MeoO_{33.6}NonOx_{3.5}AmOx_{0.7}TPP\text{-}Ox_{3.1}$	5123	1.17
P3	$MeOx_{29.0}NonOx_{7.1}$	3970	1.03
P4	$MeOx_{27.3}NonOx_{5.3}$	3470	1.03

[a] From NMR data. [b] Solvent: DMAc; RI detector; poly(methyl methacrylate) calibration.

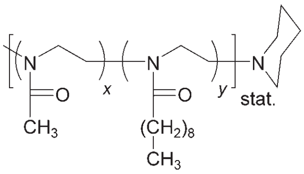
Hydroformylation of 1-octene: In the first set of experiments we investigated the nonfunctionalised copolymers **P3** (random copolymer) and **P4** (block copolymer) in the aqueous two-phase hydroformylation of 1-octene at different copolymer concentrations. As catalyst precursor we used [Rh(acac)(CO)$_2$] (acac = acetylacetonate) and the water-soluble phosphane ligand triphenylphosphane trisulfonate (TPPTS) to immobilise the catalyst in the water phase. The reaction parameters were chosen to meet industrial conditions ($T = 100$ °C, $p(CO/H_2) = 50$ bar). The ratio of ligand to rhodium was 5. The results of 1-octene hydroformylation at different copolymer concentrations are summarised in Table 2.



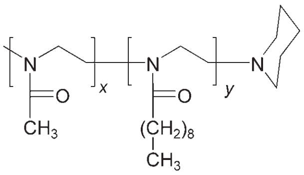
P1



P2



P3



P4

Table 2. Catalytic activities of the two-phase hydroformylation of 1-octene using nonfunctionalised poly(2-oxazoline)s **P3** and **P4** as the amphiphiles.

c_{polymer} [mol L^{-1}]	TOF [h^{-1}][a] **P3**	TOF [h^{-1}][a] **P4**
5×10^{-3}	1560	1330
4×10^{-4}	1200	640
1×10^{-5}	1120	490
1×10^{-6}	840	370
1×10^{-7}	800	210

[a] Determined by the initial formation rate of aldehydes, olefin isomerisation not taken into account; reaction conditions: $T=100$°C; $p(CO/H_2)=50$ bar; $c([Rh(acac)(CO)_2])=2\times10^{-4}$ mol L^{-1}; rhodium/TPPTS = 5; substrate/1-octene, substrate/rhodium = 10000.

In general, the random copolymer **P3** shows higher activities than the block copolymer **P4** at the same copolymer concentration. The activity of **P3** increases steadily with increasing polymer concentration with TOF numbers of 800 h^{-1} ($c_{\text{polymer}}=10^{-7}$ mol L^{-1}) up to 1560 h^{-1} ($c_{\text{polymer}}=5\times10^{-3}$ mol L^{-1}). The catalyst activity is already rather high (TOF = 800 h^{-1} at $c=10^{-7}$ mol L^{-1}), even at very low **P3** concentrations, whereas the block copolymer **P4** has almost no effect on the activity at the same concentration. However, the hydroformylation activity drastically increased from 640 to 1330 h^{-1} by increasing the concentration of **P4** from $c_{\text{polymer}}=4\times10^{-4}$ to $c_{\text{polymer}}=5\times10^{-3}$ mol L^{-1}.This effect can be ascribed to the formation of micellar aggregates in this concentration range and the increased solubility of 1-octene in water, which is also observed when using surfactants.[5]

The random copolymer **P3** on the other hand does not show a sudden increase of the hydroformylation activity. It is well known that the aggregation behaviour of random copolymers in water is much more complex. Depending on the type of copolymer studied, the results correspond well with the findings of Schulz who reported on random poly(2-oxazoline) copolymers that do not show a critical micelle concentration.[16] Instead, they seem to be able to form intramolecular aggregates even at low polymer concentrations, whereas at higher copolymer concentrations intermolecular aggregation becomes dominant. This could be one reason to explain the high hydroformylation activity as well as the low surface tension at low concentrations.

Regarding the selectivity of the hydroformylation of 1-octene, high isomerisation activity was observed with both **P3** and **P4** as surfactant (Figures 2 and 3, respectively).

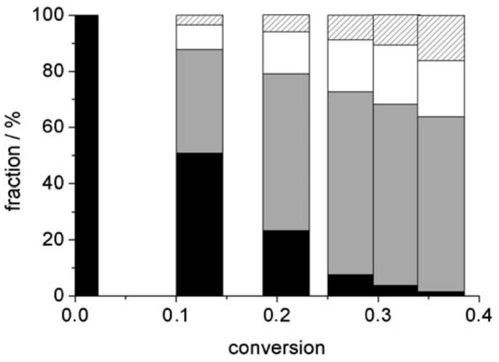


Figure 2. Product distribution as a function of conversion in the hydroformylation of 1-octene using **P3** as the amphiphile ($c_{\text{polymer}}=5\times10^{-3}$ mol L^{-1}); black = 1-octene, grey = internal octenes, white = nonanal, hashed area = isoaldehydes.

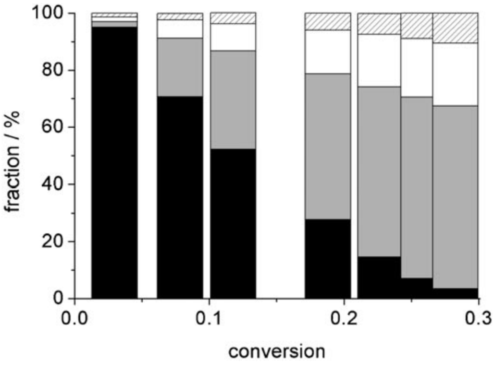


Figure 3. Product distribution as a function of conversion in the hydroformylation of 1-octene using **P4** as the amphiphile ($c_{\text{polymer}}=5\times10^{-3}$ mol L^{-1}); black = 1-octene, grey = internal octenes, white = nonanal, hashed area = isoaldehydes.

After approximately 20 % octene conversion (based on the formation of aldehydes), 60 % of 1-octene is already transformed into internal octenes in both cases. This is reflected by the *n*/iso ratios (see Figure 6, below), which drop from 3 at the beginning of the reaction to below 1 after 40 % conversion. The reason for the moderate selectivities is the low phosphane/rhodium ratio of 5:1 we applied to the hydroformylation reaction. Olefin isomerisation, which needs to be suppressed to achieve high *n*/iso ratios, can only be avoided by using either bidentate phosphanes[17] or an excess of monodentate phosphanes of up to 100 equivalents (phosphane/rhodium) to generate a sterically demanding environment around the rhodium centre as a prerequisite for high selectivities.

Although the activities in the presence of both copolymers **P3** and **P4** are still rather high, *n*/iso selectivities decrease very fast with substrate conversion to values below 1. These low values indicate that the small excess of ligands versus rhodium with a ratio of 5 is not sufficient by far to generate a sterically demanding environment around the metal centre.

In the next set of experiments we tested the amphiphilic copolymers **P1** (random) and **P2** (block copolymer). As already mentioned before, covalent linking of the triphenylphosphane moieties to the hydrophobic parts results in amphiphilic copolymers that are able to form aggregates in water. Rhodium, as the catalytically active metal, is then forced into the hydrophobic domains as a result of complexation with the hydrophobic phosphane ligands. As a consequence, the active catalyst should therefore be in direct contact with the hydrophobic substrate, which is also solubilised inside the aggregates. Reaction conditions were the same as described above ($T = 100\,°C$, $p(CO/H_2) = 50$ bar). Both copolymers show high activities, which are summarised in Table 3 for two different concentrations each. In particular, the TOF numbers of the functionalised random copolymer **P1** is significantly higher than those of the nonfunctionalised copolymers **P3** at similar amphiphile concentrations, suggesting excellent substrate/catalyst contact during hydroformylation.

Table 3. Catalytic activities of the two-phase hydroformylation of 1-octene using triphenylphosphane-functionalised poly(2-oxazolines) **P1** and **P2** as the amphiphiles.

Polymer	$c_{polymer}$ [mol L^{-1}]	TOF[a] [h^{-1}]
P1	4×10^{-4}	2200
P1	8×10^{-4}	3700
P2	4×10^{-4}	1100
P2	8×10^{-4}	1630

[a] Determined by initial formation rate of aldehydes, olefin isomerisation not taken into account; reaction conditions: $T = 100\,°C$, $p(CO/H_2) = 50$ bar, ligand/rhodium = 5, substrate: 1-octene, substrate/rhodium = 10000.

More surprising, however, are the *n*/iso selectivities observed in these hydroformylation experiments. In contrast to the nonfunctionalised copolymers **P3** and **P4**, the *n*/*iso* ratios remain almost constant at 3.0 throughout the whole catalytic process. Obviously, olefin isomerisation is efficiently suppressed within the micellar aggregates even at high substrate conversion (see Figures 4 and 5). Covalent linking of the TPP ligand to a polymer backbone is crucial for maintaining high selectivities. Amphiphilic ligands such as phosphanoethylsulfonatoalkyl thioethers still show high isomerisation ratios under similar reaction conditions and Rh/ligand ratios of 5, as can be seen in a very interesting report recently published by Oheme and co-workers.[5c]

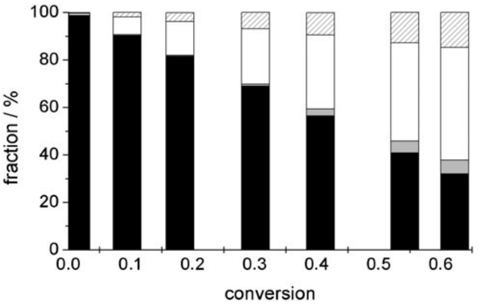


Figure 4. Product distribution as a function of conversion in the hydroformylation of 1-octene using **P3** as the amphiphilic macroligand ($c_{polymer} = 8 \times 10^{-4}$ mol L^{-1}); black = 1-octene, grey = internal octenes, white = nonanal, hashed area = isoaldehydes.

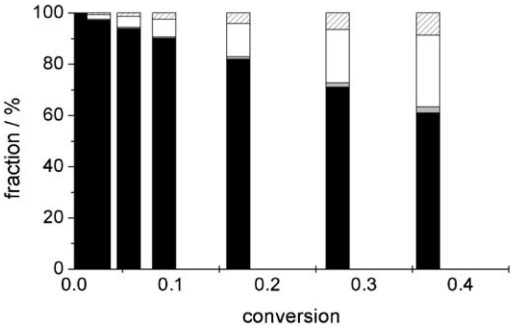


Figure 5. Product distribution as a function of conversion in the hydroformylation of 1-octene using **P4** as the amphiphilic macroligand ($c_{polymer} = 8 \times 10^{-4}$ mol L^{-1}); black = 1-octene, grey = internal octenes, white = nonanal, hashed area = isoaldehydes.

The results of *n*/iso selectivities for all four copolymer systems **P1**–**P4** are again summarised in Figure 6. According to these results, the micellar core already provides a sterically demanding environment for the rhodium catalyst at very low ligand to metal ratios of 5. These conditions lead to selectivities that can only be achieved under typical biphasic conditions with a Rh^{I}/TPPTS catalyst system when using a large excess of ligand versus metal.

To get a better appreciation for the excellent selectivities obtained in the presence of the functionalised macroligands, we carried out a homogeneous hydroformylation of 1-octene in toluene using triphenylphosphane as the ligand at different ligand/Rh ratios. The results are shown in Figure 7. At TPP/Rh ratios of 2 and 5 no effect of the conversion on the *n*/iso selectivity of the reaction products can be detected,

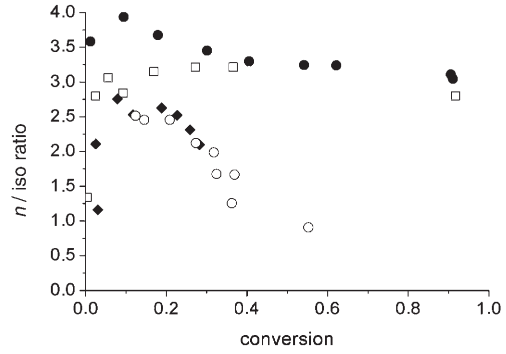


Figure 6. *n*/iso ratios as a function of conversion of the hydroformylation of 1-octene: ○ = nonfunctionalised random copolymer **P3** ($c_{polymer} = 5\times10^{-3}$ mol L^{-1}), ● = functionalised random copolymer **P1** ($c_{polymer} = 8\times10^{-4}$ mol L^{-1}), ◆ = nonfunctionalised block copolymer **P4** ($c_{polymer} = 5\times10^{-3}$ mol L^{-1}) and □ = functionalised block copolymer **P2** ($c_{polymer} = 8\times10^{-4}$ mol L^{-1}).

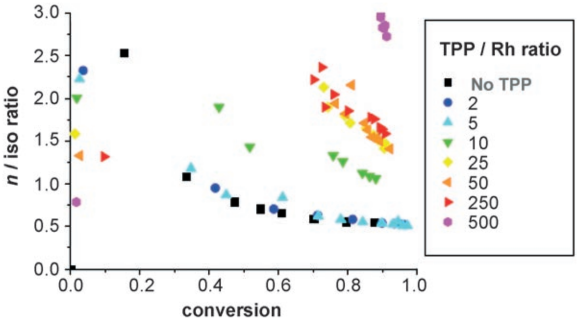


Figure 7. Homogeneous hydroformylation of 1-octene in toluene at different triphenylphosphane/rhodium ratios.

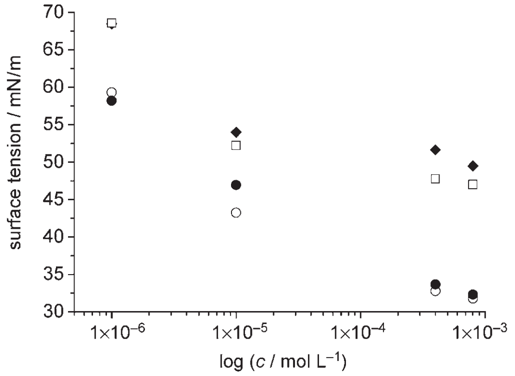


Figure 8. Results of the surface-tension measurements: ○ = nonfunctionalised random copolymer **P3**, ● = functionalised random copolymer **P1**, ◆ = nonfunctionalised block copolymer **P4**, □ = functionalised block copolymer **P2**.

and only a slight increase of the selectivity (to 1.2 and 1.7) can be detected at ligand/metal ratios of 10 and 25, respectively, at 80 % conversion. Only when using a 500-fold excess of phosphane versus rhodium were *n*/iso values of 2.9 observed at 90 % conversion.

In the last set of experiments we wanted to get a better understanding of why the random copolymers **P1** and **P3** showed higher activities in all experiments when compared with the block copolymers **P2** and **P4**. Aside from the already well-known differences in aggregate formation in aqueous media between block copolymers and random copolymers, the interfacial behaviour of these two types of copolymers at the water–hydrophobic interface will be crucial for the transport of 1-octene across the water–octene interface inside the micellar domains. Therefore, surface-tension measurements were conducted for all four copolymers at the air–water interface at different concentrations by using a ring tensiometer (see Figure 8).

The results of the surface-tension measurements show a clear difference between the random copolymers (**P3**, **P1**) and the block copolymers (**P4**, **P2**). The random copolymers reduce the surface tension much more than the corresponding block copolymers at any given concentration. The random copolymers revealed high surface activities even at very low polymer concentrations ($c = 10^{-6}$ mol L^{-1}) and lowered the surface tension to about 60 mN m^{-1}; the block copolymers had little influence on the surface tension. When the functionalised polymers (**P1**, **P2**) were compared with their nonfunctionalised counterparts (**P3**, **P4**), it was evident that the surface activity seems to be strongly dependent on the polymer architecture (random or block copolymer). However, the different copolymer compositions for both the random copolymers and the block copolymers seemed to have had very little effect on surface tension.

Recycling experiments: In the last set of experiments we wanted to study the possibility of separating the polymer-bound catalyst and reusing it in a new hydroformylation cycle. Both functionalised copolymers **P1** and **P2** were studied at a concentration of 4×10^{-4} mol L^{-1}. After the reaction was completed, both copolymers **P1** and **P2** showed distinct differences after phase separation (see Figure 9). In the presence of random copolymer **P1**, only poor phase separation occurred and the macroligand accumulated preferably at the interface and partly even in the organic phase. In contrast, phase separation occurred immediately in the presence of block copolymer **P2** after cooling down. The organic phase was nearly colourless while the macroligand seemed to be homogeneously dissolved in the aqueous phase, again reflecting the differences in interfacial behaviour of the

Figure 9. Phase separation of the aqueous biphasic 1-octene hydroformylation mixture in the presence of block copolymer **P2** (left) and the random copolymer **P1** (right).

random copolymers versus the block copolymer. The block copolymer system **P2** was further considered for recycling experiments (four cycles, each 240 min of reaction time at $T=100\,°C$ and with a synthesis gas pressure of 50 bar). The results are summarised in Table 4.

Table 4. Catalytic activities of the two-phase hydroformylation of 1-octene using **P2** as the amphiphile in four consecutive cycles.

Cycle	Conversion [%]	TOF [h^{-1}]	A_{re}[a] [%]
1	29	760	100
2	18	450	59
3	7	170	23
4	4	100	13

[a] A_{re} = activity compared with the first cycle.

The first cycle was set to 100 % activity, and the activity drops dramatically thereafter. In the fourth cycle only 13 % activity is retained compared with the first cycle, which is in excellent agreement with the recent results of Oehme and co-workers. Two reasons might account for this observation. The first possibility is that the catalyst is oxidised during recycling of the catalyst system; the second reason for the observation is related to the stability of the rhodium hydride complex. To address this problem we conducted two experiments under homogeneous conditions: in the first experiment an aqueous solution and CTAB/TPPTS/[Rh(acac)(CO)$_2$] as the catalyst system was used, and in the second, toluene as solvent and TPP/[Rh(acac)(CO)$_2$] as the hydrophobic catalyst. The reactor was cooled down after a 4 h reaction with 1-octene, depressurised, and more 1-octene was then added. Whereas the activity of the TPP/toluene mixture remained constant in the second cycle, the activity of the aqueous mixture was only 25 % compared with the first run. These results led us to the conclusion that water plays a key role in deactivating the rhodium hydride species under aqueous biphasic conditions. Obviously, the catalyst is only active under hydroformylation conditions, suggesting that catalyst recycling and reuse in the Ruhrchemie/Rhône–Poulenc process is more complex and requires more process know-how.

As an important note, it should be emphasised that the problems of catalyst recycling, when using rhodium/phosphane systems under aqueous two-phase conditions, can be overcome by using, for example, an *N*-heterocyclic carbene/rhodium complex as previously published. Simple catalyst recycling was achieved under normal laboratory conditions, and no catalyst deactivation was observed even after four cycles of aqueous two-phase hydroformylation of 1-octene.[12b]

Conclusion

A new approach to a polymer-supported catalyst for aqueous-two phase hydroformylation of 1-octene was developed. The use of an amphiphilic, water-soluble copolymer with triphenylphosphane ligands covalently attached to the polymer backbone results in aggregates in the aqueous phase, with the rhodium catalyst located in the hydrophobic domains. The substrate is also predominately solubilised in these domains during hydroformylation. Our method was able to provide the product(s) with excellent activities, with TOF numbers of up to 3700 h^{-1}, and constant *n*/iso ratios of 3.0 at remarkably low ligand/metal ratios of 5. In addition, surface-tension measurements of the random versus block copolymer indicated strong differences in their interfacial behaviour, in agreement with the catalytic activities. The simple design of the macroligands provides a novel and efficient way for the hydroformylation of long-chain alkenes under aqueous biphasic conditions, and might open new possibilities for aqueous biphasic reactions of hydrophobic substrates in general.

Experimental Section

Acronyms: 2-(5-Aminopentyl)-2-oxazoline (AmOx), *N,N*-dimethylacetamide (dmac), piperidine (pip), 2-{5-[(3-diphenylphosphano)benzamidyl]-pentyl}-2-oxazoline (tppox).

Measurements: ^1H (300.13 MHz) and ^{31}P NMR (121.50 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. Gel permeation chromatography (GPC) was carried out on a Waters GPC 510 equipped with UV and refractive index (RI) detectors using polystyrene calibration standards for the poly(2-oxazoline) samples in dmac solvent. Gas chromatography analyses were performed on a Varian CP-3380 equipped with a flame ionisation detector FID/1177, capillary column CP-Sil 8 CB (length 25 m), with helium as the mobile phase. Surface tensions were measured with a Lauda ring tensiometer TE1C.

Materials: All chemicals were purchased from Aldrich and Fluka and used, unless otherwise noted, without further purification. Water-free solvents were purchased from Fluka (dichloromethane) or dried by using standard procedures (diethyl ether, KOH molecular sieve 4 Å, BTS catalyst; acetonitrile and chlorobenzene, CaH_2). Synthesis gas ($V(CO)=50\%$, rest H_2) was purchased from Linde AG. Liquid chemicals and solvents used in the hydroformylation reactions were degassed and saturated with nitrogen.

Synthesis of polymers: A 100 mL polymerisation vessel was filled with acetonitrile (40 mL), chlorobenzene (10 mL) and methyltriflate (1 equiv) resulting in a 20–40 mmolar solution. To this solution, 2-methyl-2-oxazoline (30 equiv), 2-nonyl-2-oxazoline (**P3**, **P4**: 6 equiv; **PP1**, **PP2**: 4 equiv) and 2-[5-(amino-*tert*-butoxycarbonyl)pentyl]-2-oxazoline (**PP1**, **PP2**: 4 equiv) were added. The reaction mixture was heated to 90 °C and stirred for 12 h.

In the case of the block copolymers (**PP2**, **P4**), 2-methyl-2-oxazoline was added first; the monomers forming the second block were added after 12 h of stirring at 90 °C. The mixture was then stirred for another 12 h at 90 °C.

After cooling the solution to 40 °C, piperidine (2.5 equiv) was added as the terminating agent and the mixture was stirred for 4 h. The solvent was separated by means of rotary evaporation and the solid residue was diluted in chloroform (20 mL). Potassium carbonate (50 equiv) was added and the solution was stirred for 4 h at room temperature. The polymer was precipitated in diethyl ether, filtered and dried under reduced pressure.

*Copolymer **PP1***: Yield 3.86 g (79 %); composition (determined by ^1H NMR end-group analysis): MeOx$_{34.9}$NonOx$_{4.6}$BocOx$_{4.4}$; GPC (DMAc, RI, poly(methyl methacrylate) calibration): $M_n=6454\,g\,mol^{-1}$, $M_w=7422\,g\,mol^{-1}$, PDI = 1.15; ^1H NMR ($CDCl_3$, 300.13 MHz, 20 °C): $\delta=0.83$ (t; NonOx-CH_3), 1.21 (brs; CH_2), 1.38 (s; Boc-CH_3), 1.56 (brs;

$COCH_2CH_2$, pip-C^3H_2, pip-C^4H_2), 2.03–2.40 (m; $COCH_3$, $COCH_2$, pip-C^2H_2, Boc-NH_2–CH_2–CH_2), 2.91 (s; CH_3 end group, $Z_{CH3,C=O}$), 3.05 (brs, Boc-NH–CH_2), 3.14 (CH_3 end group, $E_{CH3,C=O}$), 3.42 (brs, CH_2 backbone), 4.87 ppm (brs; Boc-NH).

*Copolymer **PP2***: Yield 2.58 g (56 %); composition (determined by ^1H NMR end-group analysis): $MeOx_{33.6}NonOx_{3.5}BocOx_{3.8}$; GPC (DMAc, RI, poly(methyl methacrylate) calibration): $M_n = 6138\ g\,mol^{-1}$, $M_w = 6690\ g\,mol^{-1}$, PDI = 1.09; ^1H NMR ($CDCl_3$, 300.13 MHz, 20 °C): $\delta = 0.81$ (t; NonOx-CH_3), 1.19 (brs; CH_2), 1.36 (s; Boc-CH_3), 1.53 (brs; $COCH_2CH_2$, pip-C^3H_2, pip-C^4H_2), 2.01–2.27 (m; $COCH_3$, $COCH_2$, pip-C^2H_2), 2.61 (s; Boc-NH_2–CH_2–CH_2), 2.88 (s; CH_3 end group, $Z_{CH3,C=O}$), 3.00 (brs; Boc-NH–CH_2), 3.11 (CH_3 end group, $E_{CH3,C=O}$), 3.39 (brs; backbone CH_2), 4.86 ppm (brs; Boc-NH).

*Copolymer **P3***: Yield 3.05 g (72 %); composition (determined by ^1H NMR end-group analysis): $MeOx_{29.0}NonOx_{7.1}$; GPC (dmac, RI, poly(-methyl methacrylate) calibration): $M_n = 4586\ g\,mol^{-1}$, $M_w = 4733\ g\,mol^{-1}$, PDI = 1.03; ^1H NMR ($CDCl_3$, 300.13 MHz, 20 °C): $\delta = 0.90$ (t; NonOx-CH_3), 1.29 (brs; CH_2), 1.63 (brs; $COCH_2CH_2$, pip-C^3H_2, pip-C^4H_2), 2.11, 2.13, 2.17 (3×s; $COCH_3$, $COCH_2$), 2.39 (brs; pip-C^2H_2), 3.00 (s; CH_3 end group, $Z_{CH3,C=O}$), 3.08 (s; CH_3 end group, $E_{CH3,C=O}$), 3.50 ppm (brs; backbone CH_2).

*Copolymer **P4***: Yield 4.54 g (91 %); composition (determined by ^1H NMR end-group analysis): $MeOx_{27.3}NonOx_{5.3}$; GPC (DMAc, RI, poly(methyl methacrylate) calibration): $M_n = 4433\ g\,mol^{-1}$, $M_w = 4551\ g\,mol^{-1}$, PDI = 1.03; ^1H NMR ($CDCl_3$, 300.13 MHz, 20 °C): $\delta = 0.89$ (t; NonOx-CH_3), 1.27 (brs; CH_2), 1.60 (brs; $COCH_2CH_2$, pip-C^3H_2, pip-C^4H_2), 2.09, 2.12, 2.16 (3×s; $COCH_3$, $COCH_2$), 2.32 (brs; pip-C^2H_2), 2.97 (s; CH_3 end group, $Z_{CH3,C=O}$), 3.07 (s; CH_3 end group, $E_{CH3,C=O}$), 3.47 ppm (brs; backbone CH_2).

Polymer-analogous removal of Boc-groups (PP1-NH_2, PP2–NH_2): Boc-functionalised polymer **PP1** or **PP2** (1 g) was dissolved in a mixture of methanol (20 mL) and hydrochloric acid (2 mL, 37 %). The solution was stirred for 2 h at 60 °C. After cooling the solution to room temperature, potassium carbonate (1 g) was added and the suspension was stirred for another 4 h. After separating the polymer solution from excessive potassium carbonate by means of filtration, the polymer was precipitated in diethyl ether, filtered and dried under reduced pressure.

*Copolymer **PP1-NH$_2$***: Yield 2.70 g (82 %); GPC (DMAc, RI, poly(methyl methacrylate) calibration): $M_n = 6214\ g\,mol^{-1}$, PDI = 1.19; ^1H NMR ($CDCl_3$, 300.13 MHz, 20 °C): $\delta = 0.85$ (t; NonOx-CH_3), 1.23 (brs; CH_2), 1.58 (brs; $COCH_2CH_2$, pip-C^3H_2, pip-C^4H_2), 2.06–2.33 (m; $COCH_3$, $COCH_2$, pip-C^2H_2), 2.83 (brs; NH_2–CH_2, CH_3 end group, $Z_{CH3,C=O}$), 3.01 (CH_3 end group, $E_{CH3,C=O}$), 3.44 ppm (brs; CH_2 backbone).

*Copolymer **PP2-NH$_2$***: Yield 4.55 g (93 %); GPC (DMAc, RI, poly(methyl methacrylate) calibration): $M_n = 6104\ g\,mol^{-1}$, PDI = 1.18; ^1H NMR ($CDCl_3$, 300.13 MHz, 20 °C): $\delta = 0.85$ (t; nonOx-CH_3), 1.24 (brs; CH_2), 1.57 (brs; $COCH_2CH_2$, pip-C^3H_2, pip-C^4H_2), 2.06–2.38 (m; $COCH_3$, $COCH_2$, pip-C^2H_2), 2.68 (brs; NH_2–CH_2), 3.02 (CH_3 end group, $E_{CH3,C=O}$), 3.44 ppm (brs; backbone CH_2).

Synthesis of phosphane-functionalised macroligand (P1, P2): Amine-functionalised polymer **PP1-NH$_2$**, **PP2-NH$_2$** (0.4 mmol, 4 equiv of amine functions) was diluted in degassed dichloromethane (60 mL). Dicyclohexylcarbodiimide (2.9 mmol, 7.2 equiv) and 4-diphenylphosphanobenzoic acid (2.4 mmol, 6 equiv) were added and the reaction mixture was stirred at room temperature for 48 h. After addition of potassium carbonate (2 g) and stirring for another 8 h, the white solid was separated by filtration. The clear polymer solution was poured into degassed diethyl ether. The precipitate was filtered under argon atmosphere and dried under reduced pressure.

P1: Yield 2.70 g (46 %) GPC (DMAc, RI, poly(methyl methacrylate) calibration): $M_n = 5970\ g\,mol^{-1}$, PDI = 1.08; composition (determined by ^1H NMR end-group analysis): $MeOx_{34.9}NonOx_{4.6}TPPOx_{4.4}$. ^1H NMR (CD_2Cl_2, 300.13 MHz, 20 °C): $\delta = 0.87$ (t; Nonox-CH_3), 1.26 (brs; CH_2), 1.54 (brs; $COCH_2CH_2$, pip-C^3H_2, pip-C^4H_2), 2.04, 2.29 (s, brs; $COCH_3$, $COCH_2$, pip-C^2H_2), 2.60 (brs; NH_2–CH_2), 2.73 (brs; PhC(O)NH–CH_2), 2.93 (CH_3 end group, $E_{CH3,C=O}$), 3.40 (brs; CH_2 backbone), 7.00 (t; *m*-CH of benzoic acid group), 7.22 (s; phenyl CH), 7.75 ppm (d; *o*-CH of benzoic acid group); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.50 MHz, 20 °C): −4.81 ppm (s; P-phosphane).

*Copolymer **P2***: Yield 0.210 g (67 %); composition (determined by ^1H NMR end-group analysis): $MeOx_{33.6}NonOx_{3.5}AmOx_{0.7}TPPOx_{3.1}$; GPC (DMAc, RI, poly(methyl methacrylate) calibration): $M_n = 6470\ g\,mol^{-1}$, PDI = 1.17; ^1H NMR (CD_2Cl_2, 300.13 MHz, 20 °C): $\delta = 0.88$ (t; NonOx-CH_3), 1.24 (brs; CH_2), 1.55 (brs; $COCH_2CH_2$, pip-C^3H_2, pip-C^4H_2), 2.08, 2.11, 2.30 (3×s; $COCH_3$, $COCH_2$, pip-C^2H_2), 2.59 (brs; PhC(O)NH–CH_2), 2.87 (brs; NH_2–CH_2), 3.02 (CH_3 end group, $E_{CH3,C=O}$), 3.42 (brs; backbone CH_2), 6.95 (t; *m*-CH of benzoic acid group), 7.29 (s; phenyl CH), 7.71 ppm (d; *o*-CH of benzoic acid group); $^{31}P\{1H\}$ NMR ($CDCl_3$, 121.50 MHz, 20 °C): −4.77 ppm (s; P-phosphane).

Hydroformylation experiments: All experiments were carried out in a 300 mL Parr high-pressure reactor.

Aqueous two-phase experiments: The reactor was evacuated, flushed with nitrogen and filled with polymer, $[Rh(acac)(CO)_2]$ (3–10 mg, depending on polymer concentration, leading to a phosphane/rhodium ratio of 5:1), water (50 mL) and 1-octene leading to a substrate/catalyst ratio of 10000. For the case of nonfunctionalised polymers (**P3** and **P4**), triphenylphosphanotrisulfonate sodium salt was added (phosphane/rhodium ratio = 5:1). Undecane was added as the internal standard. The mixture was pressurised twice to 30 bar synthesis gas ($CO/H_2 = 1:1$) to clean all supplies before the pressure was adjusted to 50 bar with a back-pressure regulator. The autoclave was then heated to 100 °C and kept at this temperature. Samples were taken every 15 to 30 min and the products were quantified by using gas chromatography.

Homogeneous hydroformylation: The reactor was evacuated, flushed with nitrogen and filled with degassed toluene (100 mL), $[Rh(acac)(CO)_2]$ (5 mg, $4\times10^{-4}\ mol\,L^{-1}$; 1 equiv), triphenylphosphane (1–500 equiv) and 1-octene leading to a substrate/catalyst ratio of 10000. Undecane (2 mL) was added as the internal standard. The mixture was pressurised twice to 30 bar synthesis gas ($CO/H_2 = 1:1$) to clean all supplies before the pressure was adjusted to 50 bar with a back-pressure regulator. The autoclave was then heated to 100 °C and kept at this temperature. Samples were taken every 15 to 30 min and the products were quantified by using gas chromatographic analysis before the reaction was terminated after 5 h.

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[1] B. Cornils, W. A. Herrmann, R. Schlögl, C.-H. Wong, *Catalysis from A to Z*, Wiley, Weinheim, **2000**.

[2] H. Chen, Y. Li, J. Chen, P. Cheng, Y. He, X. Li, *J. Mol. Catal. A* **1999**, *149*, 1–6.

[3] a) F. Monteil, R. Queau, P. Kalck, *J. Organomet. Chem.* **1994**, *480*, 177–184; b) P. Purwanto, H. Delmas, *Catal. Today* **1995**, *24*, 135–140.

[4] a) J. P. Arhancet, M. E. Davis, J. S. Merola, B. E. Hanson, *Nature* **1989**, *339*, 454–455; b) J. P. Arhancet, M. E. Davis, J. S. Merola, B. E. Hanson, *J. Catal.* **1990**, *121*, 327–339.

[5] a) H. Chen, Y. Li, J. Chen, P. Cheng, Y. He, X. Li, *J. Mol. Catal. A* **1999**, *149*, 1–6; b) M. Li, X. Hu, H. Chen, H. J. Zheng, X. Y. Huang, Y. Z. Li, X. J. Li, *Chin. Chem. Lett.* **2004**, *15*, 1022–1023; c) E. Petzold, G. Oehme, C. Fischer, M. Frank, *J. Mol. Catal. A* **2003**, *200*, 95–103; d) C. C. Miyagawa, J. Kupka, A. Schumpe, *J. Mol. Catal. A* **2005**, *234*, 9–17.

[6] L. Leclerq, M. Sauthier, Y. Castanet, A. Mortreux, H. Bricout, E. Monflier, *Adv. Synth. Catal.* **2005**, *347*, 55–59.

[7] a) H. Ding, B. E. Hanson, T. Bartik, *Organometallics* **1994**, *13*, 3761–3763; b) B. E. Hanson, *Coord. Chem. Rev.* **1999**, *185/186*, 795–807; c) S. Bischoff, M. Kant, *Ind. Eng. Chem. Res.* **2000**, *39*, 4908–4913; d) M. Schreuder Goedheijt, B. E. Hanson, J. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* **2000**, *122*, 1650–1657.

[8] a) J. Chen, H. Alper, *J. Am. Chem. Soc.* **1997**, *119*, 893–895; b) A. N. Ajjou, H. Alper, *J. Am. Chem. Soc.* **1998**, *120*, 1466–1468.

[9] a) X. Zheng, J. Jiang, X. Liu, Z. Jin, *Catal. Today* **1998**, *44*, 175–182; b) Z Jin, X. Zheng, B. Fell, *J. Mol. Catal. A* **1997**, *116*, 55–58.

[10] I. T. Horvath, G. Kiss, R. A. Cook, J. E. Bond, P. A. Stevens, J. Rabaj, E. J. Mozeleski, *J. Am. Chem. Soc.* **1998**, *120*, 3133–3143.

[11] D. Koch, W. Leitner, *J. Am. Chem. Soc.* **1998**, *120*, 13398–13404.

[12] a) M. T. Zarka, O. Nuyken, R. Weberskirch, *Chem. Eur. J.* **2003**, *9*, 3228–3234; b) M. T. Zarka, M. Bortenschlager, K. Wurst, O. Nuyken, R. Weberskirch, *Organometallics* **2004**, *23*, 4817–4820; c) M. T. Zarka, O. Nuyken, R. Weberskirch, *Macromol. Rapid Commun.* **2004**, *25*, 858–862; d) T. Kotre, O. Nuyken, R. Weberskirch, *Macromol. Chem. Phys.* **2004**, *205*, 1187–1196; e) D. Schönfelder, K. Fischer, M. Schmidt, O. Nuyken, R. Weberskirch, *Macromolecules* **2005**, *38*, 254–262.

[13] a) S. Kobayashi, *Prog. Polym. Sci.* **1990**, *15*, 751–824; b) K. Aoi, M. Okada, *Prog. Polym. Sci.* **1996**, *21*, 151–208; c) S. Kobayashi, H. Uyuma, *J. Polym. Sci. A* **2002**, *40*, 192–209.

[14] P. Persigehl, R. Jordan, O. Nuyken, *Macromolecules* **2000**, *33*, 6977–6981.

[15] S. Cesana, J. Auernheimer, R. Jordan, H. Kessler, O. Nuyken, *Macromol. Chem. Phys.* **2006**, *207*, 183–192.

[16] R. C. Schulz, *Makromol. Chem. Macromol. Symp.* **1993**, *73*, 103–115.

[17] a) Z. Freixa, P. W. N. M. van Leeuwen, *Dalton Trans.* **2003**, *10*, 1890–1901; b) J. I. vam der Vlugt, R. vam Duren, G. D. Datema, R. den Heeten, A. Meetma, J. Fraanje, K. Goubitz, P. C. J. Kamer, P. W. N. M. van Leeuwen, D. Vogt, *Organometallics* **2005**, *24*, 5377–5382; c) H. Chen, Y. Z. Li, R. X. Li, P. M. Cheng, X. J. Li, *J. Mol. Catal. A* **2003**, *198*, 1–7.

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