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Recoverable Catalysts Noncovalently Bound to a Hyperbranched Polyelectrolyte

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Polyelectrolytes with $Ph_2P(C_6H_4\text{-}p\text{-}SO_3^-)$ counterions were prepared by ion exchange from hyperbranched polycations with a polyglycerol-based polyether scaffold and 1,2-dimethylimidazolium end groups. Upon exposing a mixture of the polyelectrolyte with $[Rh(acac)(CO)_2]$ in DMSO-d_6 to 1 atm CO/H_2, a large portion of the rhodium precursor is converted to $[(phosphine)_3Rh(H)(CO)]$. Hydroformylation of 1-hexene in methanol as a model reaction proceeds with moderate activities at 80 °C, 30 bar CO/H_2. The polyelectrolyte-bound catalyst was recovered by ultrafiltration and reused up to three times.

Introduction

Homogeneous catalysts based on soluble transition metal complexes[1] display high activities and selectivities under mild conditions in a variety of reactions. The catalytic properties can be optimized and adjusted to different substrates by variations of the ligands, most often phosphines, coordinating to the metal center. These advantages of homogeneous catalysts are opposed by the necessity of separation of the products from the catalyst after the reaction, a requirement not encountered with typical heterogeneous catalyts. Distillation as a common procedure is energy consuming to some extent, and especially for high-boiling products (or side-products) catalyst decomposition is problematic. Extraction as another common procedure most often involves destruction and subsequent regeneration of the catalyst. Thus, the development of materials combining the advantages of classical homogeneous and heterogeneous catalysts remains a challenge.

Most approaches for immobilization of metal complexes have employed microporous organic or inorganic solids. While this approach is potentially very versatile, practical use has been limited to date.[2] By comparison, aqueous two-phase catalysis is applied industrially on a large scale in the hydroformylation of propene.[3] However, aqueous two-phase catalysis requires a low, yet sufficient water-solubility of the substrates, strongly limiting its scope. Therefore, as a different strategy, binding to soluble polymers,[4] that is linear polymers[5] or dendrimers,[6,7] has found increasing interest. Ultrafiltration can be used as a mild, energy-saving method for catalyst recovery and recycling.[5b,6h,j,8] Regarding its technical viability for organic solvents, it can be noted that ultrafiltration in hydrocarbon solvents has been demonstrated in refinery operations on a large scale.[9] The majority of the approaches to attach homogeneous catalysts to soluble polymers have employed covalent

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attachment of ligands (e.g., of mono- or bidentate phosphines) to polymers. Noncovalent electrostatic binding[10] is an attractive alternative, due to a convenient synthetic accessibility of the polymer-supported catalysts and also an efficient binding that is flexible on the molecular level at the same time; that is, more than covalently bound ligands ligand-substituted counterions can move freely about the polymer chain.

Clear advantages of highly branched macromolecules by comparison to linear polymers are their low tendency for crystallization and corresponding high solubility, which is beneficial in catalyst synthesis and enables high conversions. However, for dendrimers this is contrasted by a tedious, costly synthesis of the polymer scaffold. By contrast to the ideally perfectly branched dendrimers (degree of branching 100%),[11] hyperbranched polymers[12] possess a randomly branched topology; that is, in addition to branching units they also contain considerable amounts of linear groups (degree of branching ca. 60%). Hyperbranched polyglycerol is conveniently accessible with narrow molecular weight distributions.[13] We now report on homogeneous catalysts electrostatically bound to hyperbranched polymers and on their recycling by ultrafiltration.[14]

Results and Discussion

Cationic polyelectrolytes based on a hyperbranched polyglycerol (PG) scaffold with 1,2-dimethylimidazolium (1,2DMI) moieties as cationic end groups are conveniently accessible.[15]

Exchanging the polyelectrolyte counterions by monosulfonated triphenylphosphine ligands (TPPMS = $Ph_2P(C_6H_4\text{-}p\text{-}SO_3^-)$) affords polymers with a high number of phosphine functionalities (see Figure 1), which are able to form catalytically active complexes with transition metals such as rhodium. The resulting polymer-bound complexes possess a sufficient solubility in polar organic solvents such as methanol or dichloromethane.[15] Polyelectrolytes ($PG(C_n\text{-}1,2\text{-}DMI\text{-}TPPMS)_{1.0}$) of different spacer lengths ($n = 2, 5, 7, 10$) were prepared (general nomenclature for the polyelectrolytes: PG(spacer length-type of cationic moiety-counterion)-(degree of functionalization of ends of branches with imidazolium moieties:1.0=100%)).

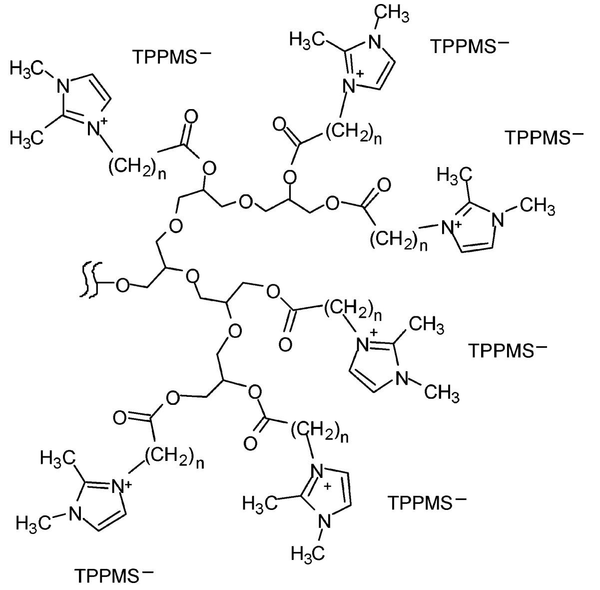

Figure 1. Structure of hyperbranched polyether-based polyelectrolytes $PG(C_n\text{-}1,2DMI\text{-}TPPMS)_{1.0}$; $n = 2, 5, 7, 10$; TPPMS = $Ph_2P(C_6H_4\text{-}p\text{-}SO_3^-)$.

Catalyst Preparation. The nonimmobilized analogue $[HRh(CO)(TPPMS)_3]$[16] (KTPPMS = potassium-(diphenylphosphino-*p*-benzenesulfonate)) was synthesized by stirring a solution of $[Rh(CO)_2(acac)]$ (acacH = pentane-2,4-dione) in methanol with 3−5 equiv of KTPPMS at elevated temperature under CO/H_2 (1:1) pressure (e.g., 80 °C/30 bar; ^{31}P NMR (methanol-d_4): 40.6 ppm, $J_{Rh,P} = 155$ Hz). After evaporating the solvent, the complex could be isolated as an amorphous red solid. Attempts of the preparation at low CO/H_2 (1:1) pressures and room temperature resulted in the formation of a material that was identified as the hydroxo complex $[(HO)Rh(CO)(KTPPMS)_2]$. The ^{31}P NMR spectrum features a doublet at 29 ppm ($J_{Rh,P} = 129$ Hz) and a characteristic CO resonance at $\nu = 1973$ cm^{-1} in the IR spectrum. However, at higher CO/H_2 pressure and elevated temperatures, this complex is converted to $[HRh(CO)(KTPPMS)_3]$. Similar behavior has been described previously by Herrmann et al. for the reaction of NaTPPTS with $[Rh(CO)_2(acac)]$ in aqueous solution (NaTPPTS = $P(C_6H_4SO_3Na)_3$).[17]

In aprotic solvents (e.g., DMSO), as expected, the formation of the hydroxo-carbonyl species was not observed under the above-mentioned conditions. A mixture of at least three complexes was detected by ^{31}P NMR, including $[HRh(CO)(KTPPMS)_3]$.

Interestingly, when the macroligands $PG(C_n\text{-}1,2DMI\text{-}TPPMS)_{1.0}$ were used instead of non-polymer-bound TPPMS with $[Rh(CO)_2(acac)]$ (P:Rh = 4), formation of the hydrido-carbonyl species with three coordinated phosphine ligands was observed to a large extent, also at room temperature and low CO/H_2 pressure (e.g., 1 bar), presumably as a consequence of the high local

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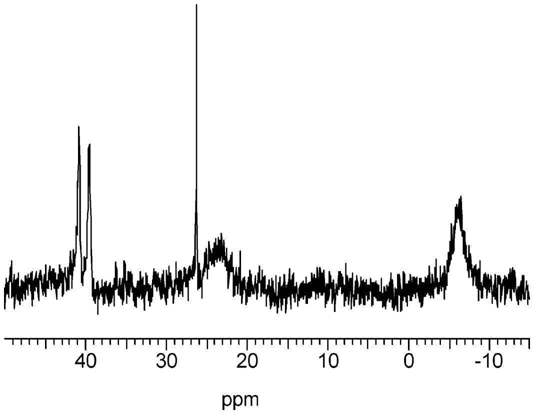
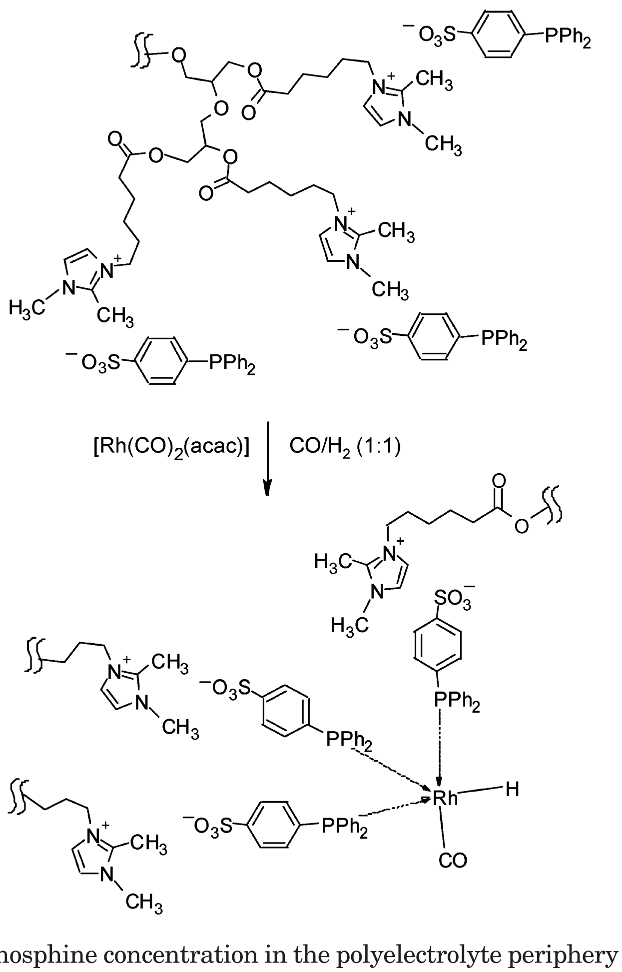


Figure 2. ^{31}P NMR (121.4 MHz, d_6-DMSO) spectrum of the in situ system [Rh(CO)$_2$(acac)]/PG(C$_5$-1,2DMI-TPPMS)$_{1.0}$ (P:Rh = 4) after stirring under CO/H$_2$ (1 atm) at room temperature for 20 min.

Scheme 1. Schematic Representation for the in Situ Formation of the Catalyst Precursor with Polymeric Ligands of the Type PG(C$_5$-1,2DMI-TPPMS)$_{1.0}$



phosphine concentration in the polyelectrolyte periphery (Scheme 1).

The P:Rh ratio used for the in situ synthesis (vide infra) of the polymer-bound catalyst system was between 4 and 10. The ^{31}P NMR spectrum of the polymer-attached catalyst (Figure 2) formed in situ shows no significant deviation vs the low molecular weight complex [HRh(CO)(KTPPMS)$_3$] (^{31}P NMR: 40.2 ppm, $^1J_{Rh,P}$ = 151 Hz).

Considering three phosphines coordinated to one rhodium atom, depending on the molecular weight of the polyelectrolyte (due to different spacer lengths), a maximum theoretical load of 0.59 to 0.49 mmol Rh/g polymer is possible. However, the maximum load was not practicable for the system PG(C$_n$-1,2DMI-TPPMS)$_{1.0}$/[Rh(CO)$_2$(acac)], as a P:Rh ratio of 3:1 resulted in precipitation of the polyelectrolyte. Ratios of at least 4:1 were required for sufficient solubility of the polymer-attached catalyst in methanol or CH$_2$Cl$_2$, allowing maximum loadings of up to 0.44 mmol Rh/g polymer.

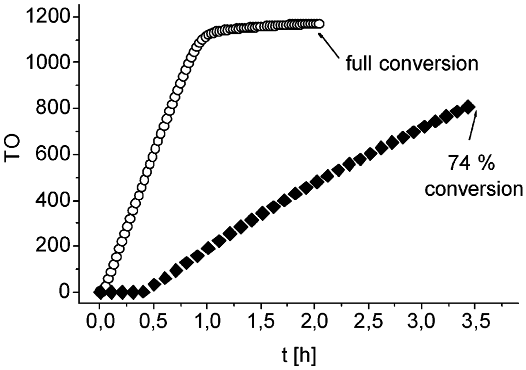


Figure 3. Catalytic activity of the free (circles) and polymer-bound (black diamonds) in situ prepared catalyst [Rh(CO)$_2$(acac)]/L (L = KTPPMS or PG(C$_n$-1, 2DMI-TPPMS)$_{1.0}$) in the hydroformylation of 1-hexene (80 °C/30 bar CO/H$_2$).

Hydroformylation. Hydroformylations were carried out in homogeneous solution using PG(C$_n$-1,2DMI-TPPMS)$_{1.0}$ as polymer-bound ligand and [Rh(CO)$_2$(acac)] as a metal precursor. For the use of the system PG-(C$_n$-1,2DMI-TPPMS)$_{1.0}$/[Rh(CO)$_2$(acac)] in recycling experiments, it can be favorable not to use the highest possible loading (P:Rh = 4) but rather higer P:Rh ratios. Due to phosphine oxidation by trace amounts of oxygen, the ligands will lose their coordinating ability, and an excess of free ligands in the initial catalyst solution, capable of coordination, could help reduce metal leaching during ultrafiltration. Thus, generally a P:Rh ratio of 10:1 was chosen for the recycling experiments.

Hydroformylation of 1-hexene was studied at 80 °C under 30 bar CO/H$_2$ (1:1) with the in situ system PG-(C$_n$-1,2DMI-TPPMS)$_{1.0}$/[Rh(CO)$_2$(acac)]. The reaction was monitored via the CO/H$_2$-uptake, measured with mass-flow meters. The polymer-bound catalysts posessed good activities in methanol (200−400 TO/h), although the activity was ca. 4 times higher when non-polymer-bound TPPMS was used as ligand, as illustrated in Figure 3.

The linear vs branched selectivity of the polymer-bound catalysts was in the range of l/b = 3−3.5, which confirms that a phosphine-coordinated rhodium complex is involved as the active species.[1] In all cases low rates of side reactions (hydrogenation, isomerization) have been observed (below 2%).

As the hydroformylation reactions were carried out in homogeneous methanol solution, mass transfer limitations should not occur. The lower activity of the polymer-attached catalyst can be related to a higher reversible inhibition of the catalytic center due to the high local phosphine concentration in the polymer, which may result in the blocking of coordination sites for the substrates to some extent.

Table 1. Hydroformylation of 1-Hexene with Polymer-Bound Rhodium-Phosphine Catalysts (entry 1 for comparison)[a]

entry	ligand	spacer	solvent	Rh, μmol	P:Rh	1-hexene, mmol	conv, %[b]	TO/h	l/b
1	nonpolym		methanol	58	10	80	92	1270	3.2
2a	polym	C_5	methanol	37	10	40	33	180	3.6
2b	polym	C_5	methanol	29	10	40	53	360	2.8
2c	polym	C_5	methanol	21	10	40	27	270	2.8
2d	polym	C_5	methanol	18	10	40	13	150	2.8
3	polym	C_2	methanol	20	10	80	22	390	2.8
4	polym	C_5	methanol	20	10	80	13	260	3.8
5	polym	C_7	methanol	20	10	80	18	320	3.8
6	polym	C_{10}	methanol	20	10	80	14	275	3.7
7	polym	C_5	THF/H_2O (8:1 v/v)	20	8	80	5	120	2.9
8	polym	C_5	1,4-dioxane/H_2O (8:1 v/v)	20	4	80	14	270	2.8

[a] Reaction conditions: 80 °C; 30 bar CO/H_2 (1:1), total reaction volume 100 mL. [b] Conversion to aldehydes (including acetals formed as secondary products by reaction with solvent in experiments carried out in methanol) as determined by GC after 2 h reaction time.

Entries 2a−2d in Table 1 summarize the results from a recycling experiment, where the catalyst was recycled three times (for details of the recyling process cf. the following section). For recycling purposes, the hydroformylation products and byproducts were separated from the polymer-bound catalyst by ultrafiltration. It seems that the catalyst has reached a constant composition after the first recycling run, as the selectivity did not change further. In contrast, the activity of the catalyst decreased in the last two runs (rhodium loss was already considered in the calculation), which can presumably be attributed to a partial oxidation of the phosphine ligands (for recycling, the catalyst solution had to be switched several times between autoclave and ultrafiltration apparatus).

To examine the influence of the P:Rh ratio on the catalyst selectivity, hydroformylations with P:Rh ratios of 4, 10, and 20 were performed. A slight enhancement of the l:b ratio from 3 to 3.5 at P:Rh = 4 to 4−5 at P:Rh = 20 was observed with the polymer-bound catalyst. The l:b ratios were generally somewhat higher than with the non-polymer-bound ligands under otherwise identical conditions, this observation supporting the suggestion that the high local P concentration in polymer-bound catalysts enhances selectivity somewhat. The activity of the complex was not affected significantly by the change of P:Rh ratio.

As mentioned above, polycations with spacer lengths of 2, 5, 7, and 10 C atoms were synthesized and used as soluble catalyst supports in hydroformylation reactions. The change of flexibility and ion density in the polymer upon spacer length variation had no significant influence on the selectivity or activity of the complex in the hydroformylation of 1-hexene (entries 3−6 in Table 1).

To avoid acetalization of the products during hydroformylation when working in methanol solution, other polar organic solvents were investigated. A strong limitation was given by the compatibility with the ultrafiltration membrane materials (polysulfone, provided by Sartorius) used for catalyst recycling. The polymer-bound complex is hardly soluble in neat acetone, THF, or 1,4-dioxane, but dissolved immediately in mixtures of the solvents with 5−10% water. In catalysis experiments with THF and 1,4-dioxane, the addition of 1-hexene (5−10 mL) resulted in a phase separation, the catalyst remaining dissolved in the water/polar solvent phase (which constitutes ca. 10% of the total volume). The hydroformylation in these biphasic systems proceeded with reasonable activities (200−300 TO/h), though the l/b selectivity was lower than in methanol (entries 7 and 8 in Table 1). A high degree of hydrogenation was observed in THF (ca. 13%), whereas the amount of side reactions remained low with 1,4-dioxane (<1%). Catalyst recovery in this system was not further investigated, but a combination of phase separation and ultrafiltration would be reasonable. The relatively small amount of the catalyst phase would allow a quick recirculation, and in contrast to the classical TPPTS-based systems, ultrafiltration offers the advantage to eliminate high-boiling condensation products, which cannot be removed by distillation.

Ultrafiltration Recovery. The effectiveness of the catalyst binding to the polyelectrolyte by ionic interactions was investigated by ultrafiltration experiments, carried out in a custom-made, semicontinuous ultrafiltration apparatus. The catalyst solution to be separated was pumped into the steel filtration cell (25 mL) fitted with a flat-sheet membrane. The content of the cell was stirred by means of a magnetic stirr bar. A constant transmembrane pressure of 10 atm was generated by continuously feeding fresh solvent. Commercially available membranes such as the MPF-50 membrane by Koch Membrane Systems (nominal MWCO = 700 Da) and polysulfone membranes from Sartorius with various molecular weight cutoffs (nominal MWCO = 5, 10, 30, and 50 kDa) were studied.

Generally, the retention R of the catalyst on a membrane can be expressed by

$$R = 1 - \frac{c_p}{c_r}$$

where c_p and c_r are the concentration of the catalyst in the permeate and retentate, respectively. In an ultrafiltration apparatus, where the solution volume in the filtration cell V_0 is kept constant by continuously supplying neat solvent of volume V_p to the solution, the retention per cell volume is given as

$$R = 1 - \frac{V_0}{V_P} \ln \frac{c_0}{c_{(VP)}}$$

where c_0 is the initial concentration of the solute in the

Table 2. Recycling of the Polymer-Attached Catalyst (PG(C5-1,2DMI-TPPMS)1.0/ [Rh(CO)$_2$(acac)]) by Ultrafiltration

	hydroformylation[a]			recycling/ultrafiltration[b]		
entry	conv, %	l/b	μmol Rh	μmol Rh in permeate	permeate vol, mL	ret/cell vol, %
1 (1st run)	33	3.6	37	1.0	260	99.73
2 (2nd run)	53	2.8	29	1.9	200	99.15
3 (3rd run)	27	2.8	21	4.9	175	96.33
4 (4th run)	13	2.8	18			

[a] Entries 2a–d in Table 1. [b] In methanol at 10 bar transmembrane pressure, PES-membrane, MWCO 10 kDa, cell volume 25 mL, flow rate ca. 23 L m^{-2} h^{-1}.

cell and $c_{(VP)}$ is the solute concentration in the cell after a solvent volume V_p was pumped through the cell.

In preliminary filtration experiments, for the membranes with MWCOs of 0.7, 5, and 10 kDa no significant difference in the separation effectiveness was observed, the retention being above 99.9% in all three cases (M_n of polyelectrolytes: 4×10^4 to 6×10^4 g mol^{-1}). The flow rates were considerably higher with the 5 and 10 kDa membranes (ca. 20–30 L m^{-2} h^{-1}). However, in all cases, the flow rates remained constant over the ultrafiltration time; that is, the membrane performance did not change.

With the polymer-attached catalyst, a retention of >99.5% related to rhodium was found (determined by AAS from filtrate and retentate solutions), whereas the non-polymer-bound catalysts passed the membrane (5 kDa by Sartorius) unhindered. A mass balance of the permeate and retentate solution showed no significant loss; that is, a concievable adsorption of polymer on the membrane surface or elsewhere is not observed. Details of a series of recycling experiments are given in Table 2.

Rhodium leaching was low in the first run, but increased considerably in the consecutive runs. A possible explanation for these findings could be an increasing oxidation of the phosphine components, presumably when the solution is handled between ultrafiltration cell and autoclave (though this was carried out under argon). If so, improved results can be expected when the polymer-bound catalyst system is used in a closed, continuously operated membrane reactor. Also a slow decomposition of the active catalyst is conceivable, as the ultrafiltrations were not performed under synthesis gas. Nevertheless, the noncovalent binding by electrostatic interactions to the hyperbranched polyelectrolyte has proven to be sufficiently effective, as the achieved retentions are comparable to those obtained with covalently attached transition metal complexes.[6j]

Summary

The functionalization of narrow molecular weight distribution hyperbranched polyelectrolytes with a sulfonated phosphine by counterion exchange represents a convenient access to well-defined polymer-attached ligands.[15] Reaction of the polyelectrolyte with [Rh(CO)$_2$(acac)] in the presence of CO/H$_2$ (1 atm) in DMSO-d_6 resulted in the conversion of a large part of the rhodium precursor to [(phosphine)$_3$Rh(H)(CO)]. In the hydroformylation of 1-hexene, a slightly reduced catalytic activity of the polymer-bound catalyst but somewhat higher linear/branched selectivities compared to the unbound complex were observed, both possibly being attributed to the high local phosphine concentration in the polymer periphery. Catalytic activity and selectivity was only little affected by the P:Rh ratio or the density/flexibility of the cationic groups. The catalyst can be recovered and recycled by ultrafiltration several times.

Experimental Section

General Procedures. All procedures, where phosphine compounds were involved, were carried out under argon (respectively CO/H$_2$ (1:1)) with degassed or freshly distilled (under argon) solvents. KTPPMS[15,18] and [Rh(CO)$_2$(acac)][19] were prepared by known methods. All other chemicals were purchased from Aldrich or Fluka and used without further purification. CO/H$_2$ was purchased from Messer-Griessheim with a CO/H$_2$ ratio of 1.

^{31}P NMR spectra were recorded in methanol-d_4 or DMSO-d_6 respectively at 298 K on a Bruker ARX 500 spectrometer operating at 202.4 MHz. The chemical shifts are referenced to external H$_3$PO$_4$. Gas chromatography was performed on a Chrompack CP9003 equipped with a 30 m CP SIL5-CB column (Ø 0.25 mm, carrier gas 30 kPa N$_2$) and a FID detector with the following program: injector temperature 270 °C; detector temperature 290 °C; 10 min isotherm at 35 °C, at 10 K/min to 250 °C, 3 min isotherm at 250 °C. Elemental analyses for C, H, N, S were measured on a VarioEL from Elementaranalysensysteme GmbH. The rhodium content was determined by a Analytik Jena Vario 6 AAS spectrometer, using the catalyst solutions (methanol) as is.

PG(C$_n$-1,2DMI-TPPMS)$_{1.0}$. Polyelectrolytes with TPPMS counterions were synthesized by ion exchange from PG(C$_n$-1,-2DMI-Br)$_{1.0}$. The synthesis of PG(C$_n$-1,2DMI-Br)$_{1.0}$-type polyelectrolytes is described in detail in ref 15. Typically, the exchange of bromide ions by TPPMS was performed as described below for the synthesis of PG(C$_2$-1,2DMI-TPPMS)$_{1.0}$: Under an argon atmosphere, at 80 °C a solution of 1.0 g (3.1 mmol functional groups) of PG(C$_2$-1,2DMI-Br)$_{1.0}$ in 5 mL of degassed water was added dropwise to a stirred solution of 1.24 g (3.25 mmol) of KTPPMS (potassium (diphenylphosphino-*p*-benzene sulfonate)) in 7 mL of degassed water. Toward the end of addition, the primarily formed precipitate remained. The mixture was stirred for an additional 2–3 h at 80 °C before cooling to room temperature. After settling of the precipitate, the water phase was carefully removed to a large extent and the residual solid was dissolved by adding 3 mL of degassed acetone (it is crucial that a few drops of water are left, as the polyelectrolyte is not soluble in pure acetone). The polymer was then reprecipitated by addition of 12 mL of water. After removing the water phase, the colorless solid was dried in vacuo to afford the product in 70–80% overall yield. Anal. Calcd (%) for $C_{2316}H_{2480}N_{159}O_{481}S_{80}P_{80}$ (45285.5 g mol^{-1}): C 61.45, H 5.52, N 4.93, S 5.64. Found: C 60.63, H 5.63, N 4.49, S 5.30.

Catalyst Preparation. In a typical procedure, the polymer-bound catalyst was prepared as follows: Under an argon atmosphere, 50 mg (82 μmol P) of PG(C$_5$-1,2DMI-TPPMS)$_{1.0}$ was dissolved in 90 mL of degassed methanol, and 5.2 mg (21 μmol Rh) of [Rh(CO)$_2$(acac)] was added to the clear solution. The immediately formed yellow solution was further stirred under CO/H$_2$ (1:1) for ca. 15 min until used for catalysis.

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Hydroformylation. Hydroformylations were carried out in a mechanically stirred stainless steel autoclave equipped with a temperature and pressure controlling unit. In a typical experiment, [Rh(CO)$_2$(acac)] and the desired equivalent of polyelectrolyte-bound phosphine were dissolved in 90 mL of methanol and the solution was purged with CO/H$_2$ for 10−15 min. The solution was then cannula-transferred to the autoclave (under CO/H$_2$), and 5−10 mL of degassed 1-hexene was added. The reactor was flushed three times with CO/H$_2$ and heated to 80 °C before pressurizing to a constant pressure of 30 bar. The CO/H$_2$ uptake during the reaction was monitored by a mass-flow metering system. After 2−3 h the autoclave was cooled to RT and the pressure released. Conversions and linear/branched ratio were determined by gas chromatography. For recycling experiments, the solution was kept under argon until transferred to the ultrafiltration device.

Ultrafiltration. Ultrafiltrations were carried out in a magnetically stirred, custom-made stainless steel cell with a volume of 25 mL (cf. Supporting Information). Polyethersulfone membranes with a molecular weight cutoff of 10 kDa supplied by Sartorius/Vivascience were used for recycling of the polymer-bound catalyst. To minimize catalyst loss during ultrafiltration, low molecular fractions of the polyelectrolytes were removed by ultrafiltration over a membrane with a higher MWCO than the one used for recycling experiments prior to catalyst preparation. After transfer of the polymer solution to the filtration cell (under argon), neat methanol (degassed) was supplied continuously to the cell by means of a dosing pump, sustaining a transmembrane pressure of 10 bar. Typically 8−10 cell volumes were filtered in one recycling experiment. The rhodium content in retentate and filtrate was determined by AAS measurements, which were performed directly from the methanolic solution.

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Supporting Information Available: Flow diagram of the ultrafiltration apparatus and scheme of the cross section of the ultrafiltration cell. This material is available free of charge via the Internet at http://pubs.acs.org.

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