A new type of highly active polymer-bound rhodium hydroformylation catalyst

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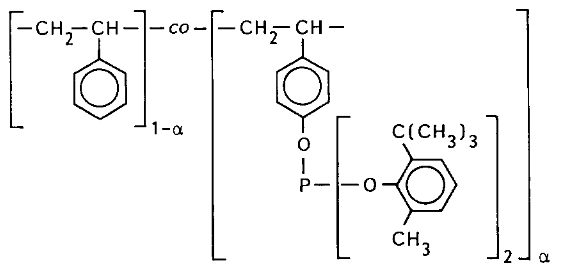
A new route of attaching phosphites to a (co)polymer chain is described. These copolymers are used for the preparation of a rhodium phosphite hydroformylation catalyst. The catalytic activity of this polymer-bound system is identical to that of the low molecular weight analogue. The catalysts show a high activity towards the hydroformylation of the otherwise unreactive cyclooctene. From spectroscopic and kinetic data, it was found that only one phosphite is coordinated to the rhodium complex in its active form. An equilibrium between this complex and an inactive complex without phosphite ligands, prohibits its use in continuous flow reactors.

(Keywords: rhodium; hydroformylation catalyst; phosphite)

INTRODUCTION

Over the last few decades much research has been done to immobilize rhodium catalysts on polymer supports[1–5]. In most studies the rhodium complex was immobilized via an aryl phosphine ligand. The drawback of this immobilization is the low stability of the phosphine ligand. Phosphines tend to degrade even in the absence of oxygen[6,7]. To avoid this problem we chose an aryl phosphite rather than a phosphine as the linkage to the polymer. The stability of aryl phosphites is much better than that of aryl phosphines. The activity of rhodium aryl phosphite complexes in hydroformylation reactions can be very high. Furthermore, it is possible to hydroformylate sterically hindered internal alkenes[8,9].

In a first step towards immobilization, the bonding of a rhodium complex to a polymer-bound aryl phosphite (**1**) was studied. The results of complexation and hydroformylation were compared with those of the low molecular weight analogue (**2**). The final aim of this research is to immobilize a suitable polymer-bound catalyst by attaching the copolymer chain to a silica surface.



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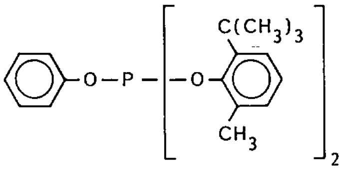

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EXPERIMENTAL

Syntheses of the copolymer support

*Poly(styrene-*co*-p-t-butoxy-carbonyl-oxystyrene).* A copolymer of styrene and *p*-t-butoxy-carbonyl-oxystyrene was prepared as described earlier[10]. The monomers used for this copolymerization were synthesized according to Fréchet *et al.*[11]. Copolymers with the following degrees of chain loading (α) were prepared: 0.07, 0.15, 0.18, 0.30, 0.48 and 0.93.

*Poly(styrene-*co*-p-hydroxystyrene).* The copolymer (6 g) obtained ($\alpha = 0.175$) was dissolved in 80 ml sulpholane and heated for 15 min at 200°C under N_2. Isobutene and CO_2 escaped from the reaction mixture, The solution was allowed to cool to 50°C and the product was precipitated in a 10-fold excess of methanol. After filtration the *p*-hydroxy copolymer was washed with methanol and dried (yield 5 g, ~95%). No t-butyl peak was detectable in the ^1H nuclear magnetic resonance (n.m.r.) spectrum and no C=O stretch vibration was present in the infra-red (i.r.) spectrum.

Functionalization of the copolymer with phosphite groups

The functionalization of the *p*-hydroxy copolymer was carried out by reaction with bis(2-methyl-6-t-butylphenyl)chloro phosphite.

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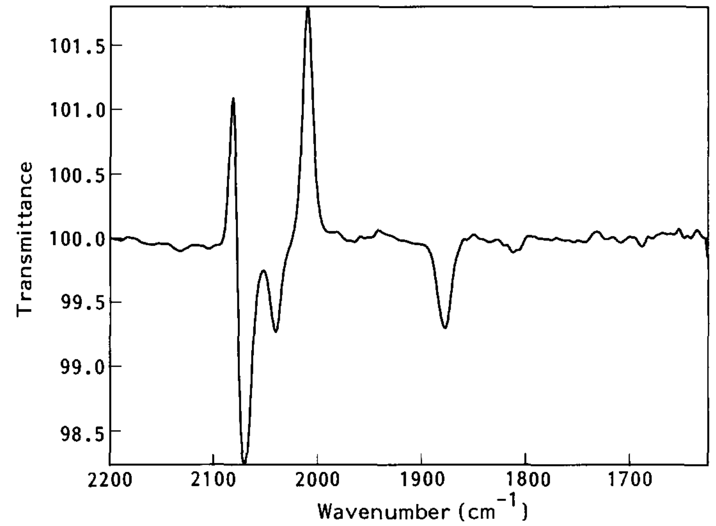


Figure 1 Transmission spectrum of rhodium complexes at 2 MPa CO/H_2 (down peaks). The spectrum at 1×10^5 Pa CO/H_2 was used as a reference (up peaks). Copolymer with $\alpha = 0.14$ was used. $[Rh]_{ov.0} = 2.4 \times 10^{-3}\ mol\ l^{-1}$, $[P]_0/[Rh]_0 = 3$, $T = 80°C$, $P_{CO}/P_{H_2} = 1$

Bis(2-methyl-6-t-butylphenyl)chloro phosphite. A solution of 200 g (1.22 mol) of 2-methyl-6-t-butylphenol and 165 ml (1.3 mol) of *N*,*N*-dimethylaniline in 500 ml toluene was heated at 50°C and 48 ml (0.55 mol) of phosphorus trichloride were added dropwise. The reaction mixture was allowed to react at 90°C for 5 h before it was cooled to room temperature. The precipitated aniline/HCl salt was filtered. The filtrate was percolated over alumina and evaporated till dryness. The raw product was recrystallized from n-hexane (yield 170 g, 0.43 mol, 80%).

*Poly(styrene-*co*-bis(2-methyl-6-t-butylphenyl)-*p*-styrylphosphite)* (**1**). The *p*-hydroxy copolymer and three equivalents of the prepared chloro phosphite were dissolved in freshly distilled tetrahydrofuran (THF) and heated at 60°C, after which an excess of lithium (2-methyl-6-t-butyl)phenolate in THF was added dropwise during 1 h. The slow addition was necessary to prevent precipitation of the lithium salt of the unreacted *p*-hydroxy copolymer. After adding the lithium phenolate the reaction mixture was refluxed for 18 h. After cooling the copolymer solution was precipitated in a 10-fold volume of methanol, filtered, washed and dried under vacuum. The copolymer was reprecipitated from 10% toluene solution in methanol, filtered, washed and dried under vacuum. This sequence was repeated once. Yield 4.9 g, ~60%; ^1H n.m.r., $CDCl_3$: δ 0.8–2.3 (backbone), δ 1.35 (s, t-butyl), δ 2.28 (s, Me), δ 6.8–7.4 (m, aromatic) ppm; ^{31}P n.m.r., $CDCl_3$: δ 143.2 ppm. From the ^1H n.m.r. spectrum α could be calculated.

The low molecular weight analogue

Bis(2-methyl-6-t-butylphenyl)phenyl phosphite (**2**). Bis(2-methyl-6-t-butylphenyl)chloro phosphite (50 g) was dissolved in 200 ml of freshly distilled THF and heated at 50°C. One equivalent of lithium phenolate in THF was added dropwise. After addition of the phenolate the reaction mixture was refluxed for 2 h. The THF was removed by evaporation and n-hexane was added. The lithium salts were filtered and the filtrate evaporated till dryness. From ^1H n.m.r. spectroscopy it became clear that some phenol was still present in the product. The product was dissolved in n-hexane and n-butyl lithium was added. The lithium phenolates formed were filtered and the product crystallized from the filtrate. Yield 11.5 g, ~20%; ^{31}P n.m.r., $CDCl_3$: δ 136 ppm (s); ^1H n.m.r., $CDCl_3$: δ 1.3 (s, t-butyl, 18H), 2.3 (s, Me, 6H), 6.3–7.2 (m, aromatic, 11H).

Catalyst precursor

Rhodium(1,5-cyclooctadiene)-2,4-pentanedionate (Rh(COD)acac). $(Rh(COD)Cl)_2$ was prepared according to Chatt and Venanzi[12]. The dimer (2.48 g, 5 mmol), 2.5 g of Na_2CO_3, 2.5 g of 2,4-pentanedione and 20 ml of water were suspended in 60 ml of CH_2Cl_2 and stirred at room temperature for 16 h. The water layer was extracted with CH_2Cl_2. The combined CH_2Cl_2 layers were evaporated till dryness. The product was crystallized from diethylether (yield 2.5 g, 80%).

Kinetic measurements

The kinetic experiments were carried out in a stainless steel autoclave of 100 ml at a pressure of 2 MPa CO/H_2 (1:1) and a temperature of 80°C. For a standard experiment the reaction vessel was charged with 20 ml of toluene, 2 ml of cyclooctene, 7.5 mg of (Rh(COD)acac) and a variable amount of phosphite **1** or **2**. During the reaction, samples were drawn and analysed with a GLC apparatus (Packard 419, SE-30 column).

Spectroscopic experiments

I.r. measurements on complexation reactions. The experiments were carried out in a stainless steel autoclave, equipped with a Morgan plunger pump and an i.r. cell with CaF_2 windows. The reaction mixture was pumped constantly through the i.r. cell. During the reaction i.r. spectra were collected with a Bruker IFS-88 i.r. spectrometer.

For all experiments a phosphite to rhodium ratio of 10 was used. Because of the strong carbonyl band of the hydroformylation product (cyclooctane carboxaldehyde) no cyclooctene was added. The temperature was kept constant at 80°C. The CO/H_2 (1:1) pressure was increased stepwise. Spectra were collected at every step. By subtracting low pressure spectra from higher pressure spectra, the changes in the rhodium complexes formed could be clearly seen (*Figure 1*).

N.m.r. measurements. A sapphire n.m.r. tube with titanium tap was used for high pressure n.m.r. experiments. The spectra were recorded on a Varian VXR-300 n.m.r. apparatus. Before measurement the samples were allowed to react for 30 min at 80°C under 2 MPa CO/H_2. For these experiments the phosphite to rhodium ratio was also 10. No cyclooctene was added.

Low pressure experiments were carried out in normal glass n.m.r. tubes.

RESULTS

Kinetics

As a standard test reaction for the catalyst the hydroformylation of cyclooctene at 80°C at 2 MPa H_2/CO was used. The major advantage of cyclooctene as a substrate is that isomerization reactions do not alter the substrate. A pseudo first-order dependence on the

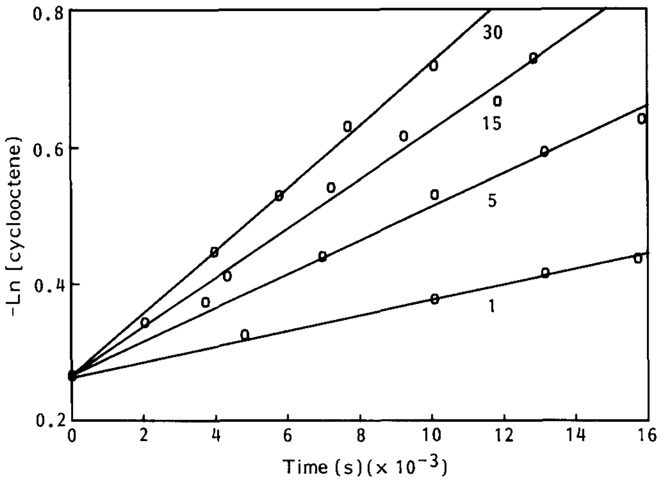


Figure 2 Plots of ln[cyclooctene] *versus* time for a polymer-bound catalyst ($\alpha = 0.29$). $[Rh] = 1.2 \times 10^{-3}$ mol l^{-1}, $T = 80$°C, pressure = 2 MPa, $P_{CO}/P_{H_2} = 1$, [P]/[Rh] as indicated

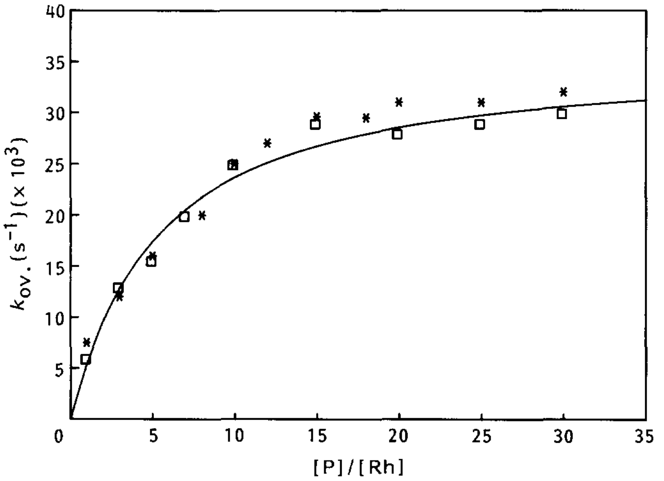


Figure 3 $k_{ov.}$ *versus* ligand to rhodium ratio for polymer-bound (*) and low molecular weight (□) catalysts. The drawn line is calculated from equation (2) with $K = 200$ l mol^{-1}. $[Rh] = 1.2 \times 10^{-3}$ mol l^{-1}, $T = 80$°C, [cyclooctene] = 0.768 mol l^{-1}, pressure = 2 MPa, $\alpha = 0.14$, $P_{CO}/P_{H_2} = 1$

substrate concentration was found as the natural logarithm of the substrate concentration against time gives a straight line (*Figure 2*). From the slope of this line we can deduce the observed overall rate constant $k_{ov.}$ as a measure of the amount of active catalyst, i.e. the catalytic activity.

The $k_{ov.}$ values were determined for polymer-bound catalysts as well as for the low molecular weight analogue. For both systems the activity increases with an increasing phosphite to rhodium ratio at constant rhodium concentration (*Figure 3*). The dependence of the $k_{ov.}$ value on the phosphite to rhodium ratio is the same for the low molecular weight analogue and the polymer-bound catalyst. The absolute values are also identical.

When the experiments with the low molecular weight analogue are carried out at higher catalyst concentrations for constant phosphite to rhodium ratio, the $k_{ov.}$ value increases, and vice versa (*Table 1*).

In polymer-bound systems, the local phosphite concentration inside separate polymer coils increases with α. In spite of this, the $k_{ov.}$ value remains the same for all α at constant phosphite and rhodium concentrations (*Figure 4*).

Spectroscopic experiments

The rhodium complex of the low molecular weight analogue **2**. To determine the nature of the rhodium complexes involved in the catalytic cycle, spectroscopic experiments were carried out. First the 'catalyst precursor' complexes were studied. ^1H n.m.r. data showed that at 1×10^5 Pa CO/H_2 pressure the acetylacetonate was still coordinated to the rhodium. The two methyl groups of the acetylacetonate appeared as three peaks. In the ^{31}P n.m.r. spectrum a doublet ($\delta = 120.5$ ppm, $J_{Rh-P} = 296$ Hz) was observed. The carbonyl area of the ^{13}C n.m.r. spectrum showed a double doublet ($\delta = 188.6$ ppm, $J_{Rh-C} = 76$ Hz and $J_{P-C} = 32.1$ Hz), and a doublet ($\delta = 184.4$ ppm, $J_{Rh-C} = 73$ Hz). Carbonyl stretch vibrations were observed in the i.r. spectrum at 2084 and 2011 cm^{-1}.

At 2 MPa CO/H_2 pressure different complexes are formed. In the ^{31}P n.m.r. spectrum a doublet is observed ($\delta = 144.3$ ppm, $J_{Rh-P} = 231$ Hz). The ^1H n.m.r. spectrum shows two peaks in the hydride area ($\delta = -9.6$ and 10.3 ppm). More information can be obtained from high pressure i.r. experiments. When the pressure is increased from 1×10^5 to 15×10^5 Pa two peaks appear at, respectively, 2075 and 2043 cm^{-1}. From 15×10^5 to 20×10^5 Pa only the peak at 2075 cm^{-1} grows further. The experiments were repeated under CO/D_2. The same peaks are observed, but now a pressure of 2 MPa D_2 and 1 MPa CO is needed before they appear. This indicates that the observed peaks must be ascribed to carbonyl vibrations.

The polymer bound complexes. The experiments carried out for the low molecular weight analogue were repeated for the polymer-bound system, starting with low pressure CO/H_2.

Table 1 $k_{ov.}$ as a function of the catalyst concentration

$[Rh]_0$ (mol l^{-1})	$k_{ov.} \times 10^3$ (s^{-1})
0.6×10^{-3}	17.3
1.2×10^{-3}	21.0
2.4×10^{-3}	28.2

$[P]_0/[Rh]_0 = 8$, [cyclooctene] = 0.768 mol l^{-1}, pressure 2 MPa, $P_{CO}/P_{H_2} = 1$, $T = 80$°C

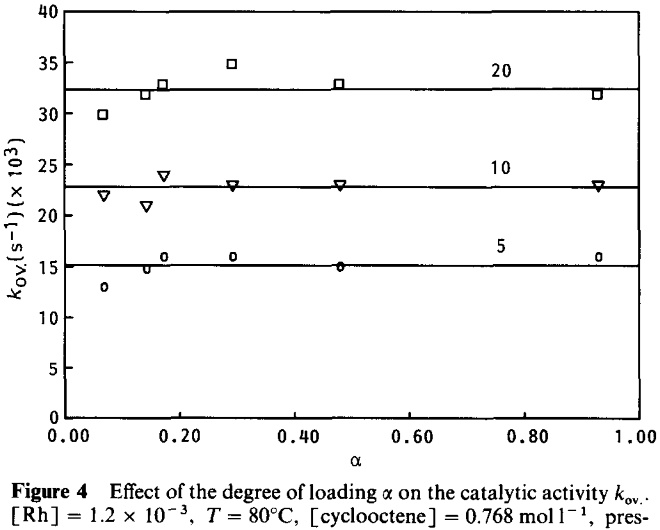


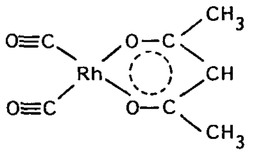
Figure 4 Effect of the degree of loading α on the catalytic activity $k_{ov.}$. $[Rh] = 1.2 \times 10^{-3}$, $T = 80$°C, [cyclooctene] = 0.768 mol l^{-1}, pressure = 2 MPa, $P_{CO}/P_{H_2} = 1$, [P]/[Rh] as indicated

The i.r. experiment showed peaks at 2083 and 2011 cm^{-1} which are almost identical to the peaks found for the low molecular analogue. The ^{31}P n.m.r. spectrum showed a broadened peak with the same shift ($\delta = 120$ ppm) as for the low molecular weight analogue. The ^{1}H n.m.r. spectrum did not reveal any useful information; the peaks were too much broadened.

The experiments at 'high' pressure were carried out for two polymer-bound phosphites with chain loading of 0.29 and 0.07, respectively. There were no significant differences between the results for these polymers. For both polymers two peaks were found in the i.r. spectrum at, respectively, 2071 and 2042 cm^{-1} (*Figure 1*). Due to a very good signal-to-noise ratio in this experiment, a peak at 1879 cm^{-1} could also be detected.

DISCUSSION

From the data in the 'low pressure' spectroscopic experiments we propose the following structures:



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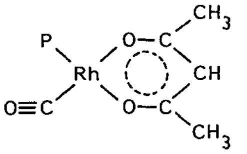

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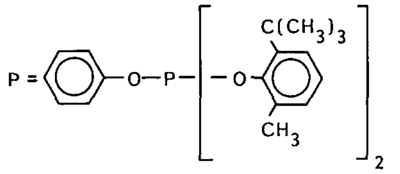
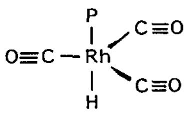


In the literature[13,14] the biscarbonyl complex (**3**) was found to have two carbonyl stretch vibrations at 2084 and 2016 cm^{-1}. We also observed the peak at 2084 cm^{-1}, while the second peak (2016 cm^{-1}) might be hidden under the peak at 2011 cm^{-1}. Structure **4** was found earlier for analogous rhodium complexes with *o*-t-butylphenyl phosphite and 2,4,6-trimethylphenyl phosphite as ligands[15]. In the ^{31}P n.m.r. spectrum doublets at, respectively, $\delta = 120$ and 118 ppm with $J_{Rh-P} =$ 293 Hz were observed for these complexes, corresponding to $\delta = 120.5$ ppm and $J_{Rh-P} = 296$ in the present study. The carbonyl stretch vibrations of these complexes are found at 2013 and 1997 cm^{-1}.

The observations in the 'high pressure' experiments show that there are two complexes formed, both with one carbonyl stretch vibration. From the isotope effect and the two hydride peaks in the ^{1}H n.m.r. spectrum, it is obvious that hydrogen is involved in the formation of these complexes. The ^{31}P n.m.r. spectrum, however, shows only one doublet so only one rhodium phosphite complex is present. The most probable structure for this complex (**5**) is:



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A second rhodium complex is present in the reaction mixture, wherein rhodium is not coordinated by phosphite. Consequently, this so-called 'free' rhodium complex is catalytically inactive. From the i.r. spectrum it appears that this complex cannot be the rhodium cluster $Rh_4(CO)_{12}$ as described by Garland and Pino[16].

In the polymer-bound system the same complexes apparently occur. The identical kinetic data agree with this conclusion. The shape of the curve of $k_{ov.}$ *versus* phosphite to rhodium ratio (*Figure 3*), however, needs further explanation.

The dependence of $k_{ov.}$ for the low molecular weight analogue on the phosphite to rhodium ratio can be explained considering the following equilibrium:

$$\underset{\text{Inactive complex}}{Rh + P} \overset{K}{\rightleftarrows} \underset{\text{Active complex}}{Rh\text{–}P}$$

Indications for the existence of such an equilibrium are found in *Table 1*. The activity increases when $[Rh]_0$ and $[P]_0$ increase, i.e. when the equilibrium shifts to the right. When this equilibrium exists, the concentration of active rhodium species can be calculated from the following equations:

$$K = \frac{[Rh\text{–}P]}{[Rh][P]} = \frac{[Rh\text{–}P]}{\{[Rh]_0 - [Rh\text{–}P]\}\{[P]_0 - [Rh\text{–}P]\}} \quad (1)$$

$$[Rh\text{–}P] = \{([Rh]_0 + [P]_0 + 1/K) - \sqrt{([Rh]_0 + [P]_0 + 1/K)^2 - 4[Rh]_0[P]_0}\}/2 \quad (2)$$

where $[Rh]_0$ and $[P]_0$ are the initial rhodium and phosphite concentrations, respectively.

The $k_{ov.}$ of the reaction is linearly related to the concentration of active rhodium complex. Equation (2) was fitted with the experimental data obtained for the low molecular weight analogue. With a complexation constant K of ~200 l mol^{-1} the theoretical curve fitted the experimental data very well (*Figure 3*).

For the polymer catalyst the system is slightly different. Below the critical overlap concentration c^* the phosphite groups are located inside separate copolymer coils. For two copolymers ($\alpha = 0.14$ and 0.29) the intrinsic viscosities ($[\eta]$) were determined by Ubbelohde viscometry at 80°C. From $c^* = 1/[\eta]$ the c^* values were calculated (*Table 2*)[17]. The c^* values of these two copolymers correspond to phosphite to rhodium ratios just above 30 in this study. Above c^* the polymer-bound phosphite groups are homogeneously distributed throughout the solution, and the value of $k_{ov.}$ of the copolymer systems is identical to that of the low molecular weight analogue. So, we can conclude that the intrinsic activities of both systems are about the same and the same holds for K.

For low ligand to rhodium ratios the phosphite groups are concentrated in small domains, i.e. the polymer coils. Consequently, the local phosphite concentration ($[P]_{loc}$) is higher than the overall phosphite concentration ($[P]_{ov.}$). Inside the copolymer coils we find phosphite-

Table 2 Intrinsic viscosities $[\eta]$ and critical overlap concentrations c^* for two different chain loadings α

α	$[\eta]$ (dl g^{-1})	c^* (g l^{-1})
0.14	0.24	41
0.29	0.33	30

bound rhodium complexes as well as phosphite-free rhodium species. Assuming that the concentrations of free rhodium species inside and outside of the coils are the same we can calculate the local concentration of active complexes ($[\mathrm{Rh{-}P}]_{\mathrm{loc}}$) from the local equilibrium:

$$\frac{[\mathrm{Rh{-}P}]_{\mathrm{loc}}}{[\mathrm{Rh}]_{\mathrm{loc}}[\mathrm{P}]_{\mathrm{loc}}} = K \quad \text{and} \quad \phi = \frac{\text{volume copolymer coils}}{\text{total reaction volume}} \tag{3}$$

$$[\mathrm{P}]_{\mathrm{loc}} = [\mathrm{P}]_{\mathrm{ov.}}/\phi = [\mathrm{P}]_{\mathrm{loc,0}} - [\mathrm{Rh{-}P}]_{\mathrm{loc}} \tag{4}$$

$$[\mathrm{Rh}]_{\mathrm{loc}} = [\mathrm{Rh}]_0 - \phi[\mathrm{Rh{-}P}]_{\mathrm{loc}} \tag{5}$$

so,

$$[\mathrm{Rh{-}P}]_{\mathrm{loc}} = \{([\mathrm{Rh}]_0 + \phi[\mathrm{P}]_{\mathrm{loc,0}} + 1/K) - \sqrt{([\mathrm{Rh}]_0 + \phi[\mathrm{P}]_{\mathrm{loc,0}} + 1/K)^2 - 4\phi[\mathrm{Rh}]_0[\mathrm{P}]_{\mathrm{loc,0}}}\} \div \div 2\phi \tag{6}$$

The overall concentration of active species $[\mathrm{Rh{-}P}]_{\mathrm{ov}} = \phi[Rh{-}\mathrm{P}]_{\mathrm{loc}}$. Substituting this and equation (4) in equation (6) gives again equation (2) for $[\mathrm{Rh{-}P}]_{\mathrm{ov.}}$ in terms of initial overall concentrations of rhodium and phosphite. Hence, no equilibrium shift is observed. Only if an active complex contained more than one phosphite per rhodium, the overall concentration of active species might be enhanced due to a stronger shift of the complexation equilibrium inside the polymer coils.

Effects of polymers on the kinetics of catalytic reactions can also be induced by enhanced substrate concentrations in polymer domains. The copolymers used in this study are linear copolymers, for which the solubility in toluene is very good. Hence, the solvent quality inside the polymer coils will be about the same as outside and substrate enrichment in the copolymer coils is not likely to occur in our system.

The overall kinetics of the copolymer-bound system in this case are identical to the overall kinetics of the low molecular weight analogue. This conclusion is in agreement with the experimental data shown in *Figure 3*. These considerations also explain why there is no clear dependence of $k_{\mathrm{ov.}}$ on the copolymer chain loading α (*Figure 4*). By changing α at constant $[\mathrm{P}]_{\mathrm{ov.0}}$ the $[\mathrm{P}]_{\mathrm{loc.0}}$ is equally changed below c^*. This does not affect the kinetics in the present system because $[\mathrm{Rh{-}P}]_{\mathrm{ov.}}$ and $k_{\mathrm{ov.}}$ only depend on the overall concentrations and not on $[\mathrm{P}]_{\mathrm{loc.0}}$.

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