Novel water soluble catalysts for hydrogenation of olefins and low molecular weight polymers in aqueous and aqueous/organic biphasic media

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Abstract

A series of carboxylated phosphines of the type $Ph_2P-(CH_2)_n-CO_2Na$, where $n = 1$, 2, 4, 5, and 7, and p- or m-$Ph_2P-C_6H_4-CO_2Na$ have been synthesized. The ligands are readily soluble in water. The water soluble complexes $[RhCl(HEXNa)_2]_2$, **1** ($HEXNa = Ph_2P-(CH_2)_5-CO_2Na$), and $[RhCl(OCTNa)_2]_2$, **2** ($OCTNa = Ph_2P-(CH_2)_7-CO_2Na$), have been prepared by the general reaction of exchange of PPh_3 in $RhCl(PPh_3)_3$ with HEXNa or OCTNa ligands. A similar phosphine exchange reaction with $Ph_2P-(CH_2)-CO_2Na$ (NaA) led to a water insoluble complex which is formulated as $Rh(PPh_3)A(NaA)$, **3**, in which NaA acts as a P-monodentate and A^- as a P,O-chelating ligand. Complexes **1** and **2** were found to be effective catalysts for hydrogenation of olefins and polybutadiene in aqueous and aqueous/organic biphasic media, respectively. With both catalysts the terminal olefins were hydrogenated much faster than the internal olefins, but an unusually enhanced hydrogenation rate was observed in the hydrogenation of the internal double bonds in 2-pentene- and 3-pentenenitriles. The catalysts show selectivity for the hydrogenation of 1,2 (vinyl) addition units over 1,4 (internal) addition units present in the polybutadiene.

Keywords: Water soluble; Rhodium; Hydrogenation; Olefins; Low molecular weight polymers

1. Introduction

The potentially significant advantages of homogeneous over heterogeneous catalysts with respect to activity and selectivity are well documented [1], but problems of separation of product(s) from the catalyst may present major obstacles in industrial applications. One solution to this problem is to utilize liquid–liquid biphasic systems in which solutions of the catalyst and of the substrate and product(s) are separated by a phase barrier [2]. The choice of water as the reaction medium with the use of water soluble metal complexes has gained increasing attention as water is non-miscible with most organic substrates used in catalytic reactions. In addition, catalysis in aqueous phase constitute safer, cheaper, and better environmental alternatives to current industrial processes using organic solvents. Thus organometallic catalysis in aqueous media has become an alternative and emerging approach in modern homogeneous catalytic reactions. The enormous interest in this

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field is apparent from the many reviews [3] and papers [4,5] that appeared in the recent literature. Several catalytic reactions have been achieved in aqueous/organic biphasic systems among which hydroformylation [6] and hydrogenation [7] of olefins provide representative examples. In fact, hydroformylation of olefins is carried out in industrial scale using a water soluble rhodium catalyst (Ruhrchemie/Rhone–Poulenc process) [8]. The success of this process reveals the potential of water soluble catalysts in other industrial applications. In most of these systems water solubilization of the metal complexes that are used as catalysts have been achieved by using water soluble phosphine ligands. Therefore much effort has been directed toward tailoring the phosphine ligands with appropriate polar substituents including carboxylate [9], ammonium [10], phosphonium [11,12], sulfonate [13], or hydroxyl [14] functions, which induce solubilization in water. Among these various water soluble phosphines reported, sulfonated phosphines or quaternized tertiary aminophosphine bearing transition metal complexes have been studied most extensively on catalytic reactions, but less work has been done on complexes containing carboxylated phosphine ligands. Due to the key role of rhodium complexes in hydrogenation, and due to our ongoing research on homogeneous hydrogenation [15], we became interested in the synthesis and study of catalytic properties of rhodium complexes containing carboxylated phosphine ligands.

Although two-phase catalysis with water soluble metal complexes has been successfully carried out with smaller alkenes, the rate of such reactions with higher alkenes may become extremely slow due to phase transfer limitations. Several attempts have been made in the past to overcome this problem which include the use of quaternary ammonium or phosphonium salts in place of the trisodium salt of the trisulfonated triphenylphosphine (TPPTS) [16], and the use of supported aqueous phase catalysts (SAP catalysts). In the latter approach the water soluble

catalyst is immobilized in a supported aqueous phase on a high surface area hydrophilic solid [5,17]. Another development in enhancing catalysis in biphasic aqueous/organic systems involves the use of a 'promoter ligand' [18]. This ligand is soluble in the organic phase but insoluble in the aqueous phase, and will bind to the water-soluble organometallic catalyst thereby increasing the catalyst concentration at the interface. A different and a more promising approach involves use of catalysts containing surface active phosphine ligands [19–23]. Significant rate enhancements in hydroformylation of higher olefins have been observed in such systems.

In an attempt to determine the effect of ligand chain length on the surface activity and hence on the catalyst properties we prepared a series of carboxylated phosphine ligands of the type $Ph_2P-(CH_2)_n-CO_2Na$, where $n = 1$, ETHNa; 2, PROPANa; 4, PENTNa; 5, HEXNa; or 7, OCTNa, and para- or meta-$Ph_2P-C_6H_4-CO_2Na$ (p- or m-BENZNa). In this paper we report the synthesis and characterization of the above-mentioned ligands and their rhodium complexes. The catalytic activities of the water soluble complexes $[RhCl(HEXNa)_2]_2$, 1, and $[RhCl(OCTNa)_2]_2$, 2, in hydrogenation of simple alkenes and polybutadiene in aqueous and aqueous/organic biphasic media are also presented.

2. Experimental

All syntheses were performed under prepurified zero-oxygen nitrogen using standard Schlenk techniques.

2.1. Materials

Reagent grade solvents were used as supplied and were degassed before use. Distilled deionized water was used in all instances where water is specified and is degassed prior to use. Oxygen-free hydrogen gas was used in hydrogena-

Table 1
^{31}P NMR data of carboxylated phosphines and their rhodium complexes [a]

Compound	Abbreviation	δ [c]	$^1J_{Rh-P}$ (Hz)	J_{P-P} (Hz)
$Ph_2P-(CH_2)-CO_2Na$	ETHNa	− 18.29		
$Ph_2P-(CH_2)_2-CO_2Na$	PROPANa	− 16.24		
$Ph_2P-(CH_2)_4-CO_2Na$	PENTNa	− 16.34		
$Ph_2P-(CH_2)_5-CO_2Na$	HEXNa	− 16.72		
$Ph_2P-(CH_2)_7-CO_2Na$	OCTNa	− 16.82		
p-$Ph_2P-(C_6H_4)-CO_2Na$	p-BENZNa	− 6.21		
m-$Ph_2P-(C_6H_4)-CO_2Na$	m-BENZNa	− 6.45		
$[RhCl(HEXNa)_2]_2$	1	17.00 (d)	140.89	
$[RhCl(OCTNa)_2]_2$	2	17.78 (d)	151.17	
$Rh(Ph_2P-CH_2-CO_2)(ETHNA)(PPh_3)$	3 [b]	27.52 (ddd)	146	314, 38
		27.84 (ddd)	145	314, 41
		54.43 (dt)	178	39

[a] The spectra are recorded in D_2O at 298 K.
[b] In $CDCl_3$.
[c] In ppm relative to external H_3PO_4; downfield shifts positive; d = doublet, ddd = doublet of doublet of doublets, dt = doublet of triplets.

tion experiments. The alkene substrates were purified by passing through a neutral alumina column. The polybutadiene used in this study (obtained from Scientific Polymer Products) contained 40% vinyl and 30% *trans*-1,4 units and had a $\overline{M}_n$ of 900.

2.2. Synthesis of phosphino carboxylic ligands

The ligands $Ph_2P-(CH_2)_n-COONa$ ($n = 1$ or 2) were synthesized following a published procedure [24]. The same procedure was extended with minor modifications to make ligands where $n = 4$, 5, or 7, and *para*- or *meta*-$Ph_2P-C_6H_4-CO_2Na$ ligands. A degassed solution of 50% KOH (50 mmol) was added to a solution of diphenylphosphine (20 mmol) in dimethyl sulfoxide (40 mL) at 20°C, with stirring. A solution of ω-chloro or ω-bromocarboxylic acid (20 mmol) in dimethyl sulfoxide (5 mL) was then added dropwise. After stirring overnight, the solution was diluted with water (100 mL) and washed with toluene. The aqueous solution was acidified by dropwise addition of 2 M HCl with vigorous stirring. The phosphino carboxylic acid that precipitated out was filtered and washed with water and vacuum dried (note: if the acid is added too quickly or if the stirring is too slow the product comes off as

an oil). A solution of the acid in ethanol was made basic with ethanolic sodium hydroxide, and ether was added to precipitate the Na-salt of the phosphino carboxylic acid. The final product was filtered, washed with ether and vacuum dried. Yield 30–60% (based on the ω-halo acid used). The ligands are characterized by NMR spectroscopy (Table 1).

2.3. Synthesis of rhodium complexes

In a typical experiment $Ph_2P-(CH_2)_n-CO_2Na$ (1.5 mmol) and $RhCl(PPh_3)_3$ [25] (0.5 mmol) were added to a solvent mixture containing CH_2Cl_2 (20 mL) and tetrahydrofuran (10 mL) and was refluxed for 30 min. After cooling to room temperature the solvent was removed under vacuum and the orange–brown residue was dissolved in water (30 mL). The resultant turbid solution was filtered through celite, and the clear red–brown filtrate was evaporated to dryness to give a orange–brown solid. Following the above procedure the water soluble complexes $[RhCl(HEXNa)_2]_2$, 1, and $[RhCl(OCTNa)_2]_2$, 2, were obtained in 62% and 80% yields, respectively. The complexes are characterized by NMR spectroscopy (Table 1).

$Rh(Ph_2P-CH_2-CO_2)(ETHNa)(PPh_3)$, 3: A suspension of $Ph_2P-CH_2-CO_2Na$ (0.8 mmol)

and $RhCl(PPh_3)_3$ (0.25 mmol) in a mixture of THF (20 mL) and CH_2Cl_2 (30 mL) was refluxed for 45 min. After cooling to room temperature the solvent was removed under vacuum and the resultant orange–brown residue is taken up in a mixture of water (30 mL) and THF (10 mL) to give a bright-yellow precipitate with a pale-yellow solution. After stirring the mixture overnight, the yellow product was filtered, washed with water and ether and vacuum dried. Yield 68%. ^1H NMR ($CDCl_3$): $\delta = 1.81$ (t, H_a, $J_{P-H} = 6.3$ Hz), 3.20 (d, H_c, $J_{P-H} = 9.3$ Hz), 3.75 (t, H_b, $J_{P-H} = 6.2$ Hz), 6.7–7.9 (m, phenyl). The ^{31}P NMR data are listed in Table 1.

2.4. Instrumentation

GC analysis were performed on a Perkin Elmer Auto System gas chromatograph equipped with a flame ionization detector. The separations were accomplished with a 30 m × 0.322 cm DB-1 column. The ^1H NMR spectra were run on a Bruker AM-250 or a Bruker AMX-500 spectrometer, and the ^{31}P spectra (all ^1H decoupled) on a Bruker AC-200 spectrometer.

2.5. Hydrogenation reactions

All the reactions were carried out in a stainless steel autoclave equipped with catalyst addition and sampling devices. In a typical run, 80 mL of water and 4–5 g of organic substrate were added to a 250 mL glass liner (with polybutadiene (PBD), 2 g of polymer dissolved in 10 mL of toluene was added to 80 mL water). The catalyst was weighed into a glass bucket and placed in the catalyst addition device. The glass liner was then placed in the autoclave and the autoclave was assembled. After flushing with hydrogen three times, the mixture was degassed by bubbling H_2 for 15 min. The reaction system is then heated to the required temperature with agitation under 0.34 MPa hydrogen. After the temperature equilibrium is reached the bucket containing the cata-

lyst is dropped to the solution by pressurizing the catalyst addition device to the reaction pressure. Hydrogen was introduced into the autoclave when required to maintain a constant reaction pressure throughout the reaction period. Samples were withdrawn periodically from the reactor, which were extracted with toluene or chlorobenzene. The organic products in toluene extracts were then analyzed by GC. With PBD, the toluene extracts were dried under vacuum and the residue was dissolved in $CDCl_3$, and analyzed by ^1H NMR spectroscopy. The % hydrogenation of the polymer was calculated from the NMR integrations.

3. Results and discussion

3.1. Catalyst synthesis and characterization

The classical method of preparing the Wilkinson-type rhodium complexes involving reduction of $RhCl_3$ by excess of phosphine was attempted with the carboxylated phosphines used in the present work. These reactions were carried out in water as well as in methanol/water mixtures, both at room temperature and under reflux temperatures. But none of these reactions resulted in a hydrosoluble rhodium complex. As revealed from ^{31}P NMR spectroscopy the only phosphorus containing product that was present in the reaction mixture was the oxide of the corresponding carboxylated phosphine used in the reaction. Similar oxidation of phosphines by Rh(III) in water in the absence of oxygen has been observed between TPPTS ligand (TPPTS $= P(m\text{-}C_6H_4SO_3Na)_3$) and $RhCl_3$ [26]. Water soluble analogues of the Wilkinson complex were successfully synthesized by employing direct exchange of the triphenylphosphine groups in $RhCl(PPh_3)_3$ for carboxylated phosphines. The reaction was carried out in a mixture of organic solvents (CH_2Cl_2 and THF) in which the precursor $RhCl(PPh_3)_3$ is readily soluble and the carboxylated phosphine is marginally soluble. The reaction was carried out with a

series of carboxylated phosphines of the type $Ph_2P-(CH_2)_n-CO_2Na$ where $n = 1, 2, 4, 5,$ or 7, and *para-* or *meta-*$Ph_2P-(C_6H_4)-CO_2Na$. However, water soluble rhodium complexes could only be obtained with HEXNa and OCTNa ligands. The complexes were characterized by ^{31}P NMR spectroscopy and are formulated as chloride bridged dimers $[RhCl(HEXNa)_2]_2$, **1**, and $[RhCl(OCTNa)_2]_2$, **2**, respectively. The ^{31}P NMR data of **1** and **2** (Table 1) are comparable with those reported for the previously known organosoluble complexes $[RhCl(PR_3)_2]_2$ (R = Ph, δ: 51.9, d, $J_{Rh-P} = 193.2$ Hz; R = *p*-tolyl, $\delta = 49.5$, d, $J_{Rh-P} = 196$ Hz) [27,28]. Neither **1** nor **2** react with excess of the respective ligands to form the corresponding $RhCl(HEXNa)_3$ or $RhCl(OCTNa)_3$ complexes. This contrasts the behavior shown by analogous $[RhCl(PR)_2]_2$ complexes (R = Ph [25], or *p*-tolyl [28]). Reaction of $RhCl(PPh_3)_3$ with $Ph_2P-(CH_2)-CO_2Na$ led to a organosoluble complex **3**, which is formulated based on its ^{31}P (Table 1) and ^{1}H NMR spectroscopic data, as containing a *P,O*-chelated and a *P*-monodentate ETHNa ligand. The observed ^{1}H NMR spectroscopic data of **3** correspond well with those reported for the structurally characterized Rh(I) complex $Rh(CO)A(HA)$, where $A = P,O$-chelating $Ph_2P-CH_2-CO_2^-$, and $HA = Ph_2P-CH_2-COOH$ [29].

3
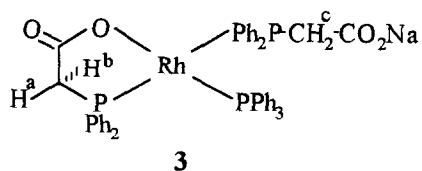
The water insolubility of **3** could be explained by invoking fluxionality of ETHNa ligand between chelated and pendent form in solution. Phosphine exchange reaction between $RhCl(PPh_3)_3$ and $Ph_2P-(CH_2)_n-CO_2Na$ ($n = 2$ or 4) and *p*- and *m*-BENZNa ligands resulted in water insoluble orange–brown material. The ^{31}P NMR spectra of the organo-soluble materials

resulted from each of these reactions showed a mixture of products, and none of them could be characterized or isolated.

3.2. Catalytic hydrogenations

The catalytic activity of the two water soluble compounds **1** and **2** in hydrogenation of olefins and polybutadiene (PBD) were investigated. The olefin hydrogenation reactions were carried out in water without any added organic solvents. The results (Table 2) show that both **1** and **2** are catalytically active in olefin hydrogenations, with **1** having a superior activity with most of the substrates studied in the present work. The only difference between the two catalysts being the chain length of the carboxylated ligand the higher activity of **1** could be attributed to the shorter methylene spacer between phosphine and carboxylic moieties in HEXNa ligand. Although similar effects of ligand chain length on catalyst activity have been previously reported [11], where it is suggested that the formation of stable micelles in the systems using catalysts containing longer chain lengths may hamper the catalyst activity, the present data are not suffice to reach a conclusion.

After the hydrogenation reactions, the catalyst remained in the aqueous layer while the organic substrates and products were in the organic phase. This was evident from the pale-yellow aqueous and colorless organic phases obtained after the reaction. However, in styrene and α-methylstyrene hydrogenations the organic layer was orange and the aqueous layer was colorless after the reaction, thus in these systems rhodium is extracted into the organic phase possibly by forming arene–Rh complexes. Some emulsification was seen between the organic and the aqueous phases after the hydrogenation reactions carried out with catalysts **1** and **2** with all the different substrates studied. This was significantly different from the hydrogenations of some of the substrates

Table 2
Catalytic hydrogenation of olefins in water with $[RhCl(HEXNa)_2]_2$, **1**, and $[RhCl(OCTNa)_2]_2$, **2**, complexes [a]

Run	Substrate	Product	Yield (%) [c]		Turnover frequency [d]	
			with **1**	with **2**	with **1**	with **2**
1	1-octene [b]	*n*-octane	94	23	1880	460
2	1-decene [b]	*n*-decene	92 (2 h)	12 (2 h)	920	120
3	styrene [b]	ethylbenzene	100	93	2000	1860
4	α-methylstyrene	isopropylbenzene	15	34	300	680
5	*trans*-3-pentenenitrile	valeronitrile	99	88	1980	1760
6	*cis*-2-pentenenitrile	valeronitrile	99 (15 m)	85 (15 m)	7920	6800
7	*cis*-2-heptene	heptane	41	16	820	320
8	*trans*-2-heptene	heptane	33	7	660	140
9	cyclooctene	cyclooctane	13	19	260	380

[a] Reaction conditions: catalyst $= 1 \times 10^{-5}$ mol (of the dimer), olefin $= 0.04$ mol, solvent $= 80$ mL water, temperature $= 90°C$, $H_2 = 4$ MPa.
[b] At 50°C.
[c] Reported for 1 h reaction time period, unless otherwise indicated.
[d] Number of moles of olefin reduced per mole of rhodium in 1 h.

carried out with $RhCl(TPPMS)_3$ (TPPMS = monosulfonated triphenylphosphine) under identical conditions where little or no emulsification was seen. Thus it is evident that the complexes **1** and **2** have surface active properties rendered by the amphiphilic HEXNa and OCTNa ligands.

From the results (Table 2) it is clear that the overall activity of **1** and **2** follow the order: terminal olefins > internal olefins > disubstituted olefins > cyclic olefins. However, the internal double bonds in the pentenenitriles were hydrogenated much faster, and thus deviate from the above general order. A remarkably enhanced activity of *cis*-2-pentenenitrile over *trans*-3-pentenenitrile is also observed. This could be explained by taking into account the steric effects exerted by the *cis*- versus *trans*-double bonds (*cis*-double bonds are readily reduced with most of the catalysts), or the electronic effects exerted by the nitrile group, or a combination of both factors. However, the comparable activity of *cis*-2-heptene and *trans*-2-heptene tend to suggest that the electronic effects are more important, which is specially evident in *cis*-2-pentenenitrile hydrogenation where the double bond is conjugated to the nitrile group. Hydrogenation of the nitrile group

Table 3
Catalytic hydrogenation of olefins in water with $[RhCl(HEXNa)_2]_2$, **1**, and $[RhCl(OCTNa)_2]_2$, **2**, complexes: influence of added ligand to the reaction mixture [a]

Substrate	Catalyst	% hydrogenation [b]		Turnover frequency [d]	
		without added ligand	with added ligand [c]	without added ligand	with added ligand [c]
1-decene	**1**	92 (2 h)	3 (4 h) [1.5 eq]	920	15 [1.5 eq]
styrene	**1**	100	54 [1 eq]	2000	1080 [1 eq]
styrene	**2**	93	40 [1 eq]	1860	800 [1 eq]
			9 [2 eq]		180 [2 eq]

[a] The reaction conditions are same as in Table 2; the experiments were done at 50°C.
[b] For 1 h reaction time period unless otherwise indicated.
[c] Reported for the ligand/catalyst combinations of HEXNa/**1** and OCTNa/**2**, respectively; the amount of ligand added is indicated in square brackets as number of equivalents per rhodium.
[d] Number of moles of olefin reduced per mole of rhodium in 1 h.

Table 4
^{1}H NMR spectroscopic analysis for the hydrogenation of polybutadiene (PBD) with [RhCl(HEXNa)$_2$]$_2$, 1 [a]

Time (h)	% hydrogenation	Area at 4.9 ppm [b]	Area at 5.4 ppm [c]	% 1,2 addition units
0	0	15	30	40
1	32	9	19	38
2	59	3	16	17
3	63	1	8	12
4	72	0.5	8.5	6
6	84	0	6	0

[a] Reaction conditions: catalyst = 1 × 10^{-5} mol (of the dimer), PBD = 2 g (units of unsaturation = 0.04 mol, solvent = 10 mL toluene + 80 mL H$_2$O, temperature = 100°C, H$_2$ = 5.5 MPa.
[b] =CH$_2$ protons.
[c] =CH– protons.

in the penetenenitriles were not observed under the reaction conditions.

A significant decrease in catalytic activities of both 1 and 2 was observed with the addition of the respective free carboxylated phosphine ligands to the reaction medium. The effect of added ligand on the catalytic activity is demonstrated with 1-decene and styrene hydrogenation experiments, and the results are summarized in Table 3. Presumably this reduced activity is due to a competition between the added free ligand and the olefin for a coordination site on the rhodium, which may lead to a retardation in the activation of the reaction. A similar effect of added ligand on catalytic hydrogenation of olefin has been observed with [(NBD)Rh(n-PHOPHOS)$_2$]$^{3+}$ (NBD = norbornadiene; n-PHOPHOS = [Ph$_2$P–(CH$_2$)$_n$–PMe$_3$]NO$_3$; n = 2 or 3) complexes [11].

The catalytic activities of 1 and 2 in hydrogenation of polybutadiene were studied in water (80 mL) and toluene (20 mL) solvent mixture. The polybutadiene with a $\overline{M}_n$ of 900 was used in this study, and it contained 30% trans 1,4, 30% cis 1,4, and 40% vinyl addition units. The samples withdrawn periodically during the reaction were analyzed by ^{1}H NMR spectroscopy to monitor the extent of hydrogenation, and the hydrogenation of 1,2 versus 1,4 addition units. In the ^{1}H NMR spectrum of PBD (CDCl$_3$) the aliphatic proton signals appear in the 1.3–2.6 ppm region and the vinylic protons from the 1,2-PBD units are at 4.9 ppm. The olefinic

protons from 1,2-PBD and both cis- and trans-1,4-PBD units appear at 5.4 ppm. The ^{1}H NMR spectra of partially hydrogenated PBD show new peaks at 0.9 ppm (m, CH$_3$ of hydrogenated 1,2-PBD units) and 1.3 ppm (olefinic protons of hydrogenated 1,2 and 1,4-PBD units), and the preferential hydrogenation of pendant vinyl units over 1,4 addition units is revealed by the decreasing intensity ratio of vinyl/olefin proton resonances with increasing extent of hydrogenation. The results obtained with catalyst 1 are shown in Table 4, and the results obtained with both 1 and 2 are summarized in Table 5 for comparison. From the results (Table 5) it is clear that 1 is more active than 2 in polybutadiene hydrogenation. With both catalysts the 1,2 (vinyl) addition units are selectively hydrogenated over the 1,4 (internal) addition units in PBD. This result is consistent with the observed selectivities of the two catalysts in simple alkene hydrogenation. Extension of hydrogenation

Table 5
Summary of results on hydrogenation of polybutadiene with [RhCl(HEXNa)$_2$]$_2$, 1, and [RhCl(OCTNa)$_2$]$_2$, 2, complexes [a]

Time (h)	% hydrogenation		% 1,2 addition units	
	with 1	with 2	with 1	with 2
0	0	0	40	40
1	32	23	38	39
2	59	34	17	34
3	63	44	12	30
4	72	—	6	—
6	84	65	0	13

[a] The reaction conditions are same as in Table 4.

studies to other polymers such as styrene–butadiene rubber (SBR) and nitrile–butadiene rubber (NBR) are currently in progress.

Acknowledgements

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