

# The syntheses and activities of polystyrene-supported olefin metathesis catalysts based on $\text{Cl}_2(\text{PR}_3)_2\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$ <sup>☆</sup>

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## Abstract

A series of olefin metathesis catalysts based on the  $\text{Cl}_2(\text{PR}_3)_2\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$  olefin metathesis catalysts have been attached to a 2% cross-linked polystyrene–divinylbenzene solid support. We have carried out a comparative activity study of these solid-phase catalysts and their homogeneous analogs and demonstrated that the lifetime of the supported ruthenium complexes can be extended through recycling and re-using the supported phase catalyst. These solid-phase catalysts constitute the first example of a polymer-supported well-defined olefin metathesis catalyst that produces living polymers in solution.

**Keywords:** Ruthenium; Olefin metathesis catalyst; Polystyrene supported catalysts

## 1. Introduction

The use of polymers as supports in organometallic catalysis is well documented and has been extensively reviewed [1,2]. In contrast with the majority of traditional metal oxide supports, lightly cross-linked (i.e. 2%) polymer substrates such as polystyrene (PS)–divinylbenzene (DVB) offer a means to “heterogenize” well-defined discrete homogeneous organometallic complexes directly with the retention of all the ligand environment characteristics around the metal centers. As such, polymer-supported organometallic catalysts combine both the chemical activity and the tunability of the homogeneous metal complexes and the stability and ease of separation–recovery afforded by traditional heterogeneous catalysts. Among the polymer-supported organometallic catalysts investigated, the most popular have been those based on the noble metals such as rhodium and platinum hydro-addition catalysts since in these cases the recovery and re-use of these expensive

metal complexes are highly desirable. Although polymer-supported Mo and W catalysts of the first generation (i.e. non-carbene multicomponent systems) have been found to possess olefin metathesis activities [3,4], to the best of our knowledge there has been no report of single-component well-defined olefin metathesis catalysts being attached to a polymer support.

Recently, we reported the syntheses of the ruthenium vinylcarbene metathesis catalysts  $\text{Cl}_2(\text{PR}_3)_2\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$  ( $\text{R} = \text{Ph}$  (**1**) [5] or  $\text{Cy}$  (**2**) [6]) which can catalyze the ring-opening metathesis polymerization (ROMP) of cyclic olefins and the metathesis of acyclic olefins. Subsequently, these catalysts have found a variety of applications in both polymer chemistry [7–10] and organic synthesis [8,9,11–15]. In particular, both **1** and **2** have been shown to catalyze the living ROMP of several cyclic monomers [5,8,16]. In the interest of developing methods to recover and re-use these noble metalcarbene catalysts as well as to prepare large quantities of monodispersed polymers on a support (much in the same manner that peptide synthesis is currently being carried out on Merrifield [17] resins), we synthesized a series of PS–DVB-supported ruthenium vinylcarbene catalysts and explored their metathesis activities.

<sup>☆</sup> Dedicated to Professor Hans-H. Brintzinger on the occasion of his 60th birthday.

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## 2. Results and discussion

### 2.1. The syntheses of polystyrene–divinylbenzene-supported ruthenium vinylcarbene olefin metathesis catalysts

The ability of **1** to exchange its phosphine ligands with a variety of phosphines have allowed the convenient syntheses of several PS–DVB-supported ruthenium bis-phosphine vinylcarbene catalyst (Eq. (1)–(3)). Thus a solution of **1** will readily transferred the  $\text{Cl}_2\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$  moiety onto a variety of 2%-cross-linked phosphine-functionalized PS–DVB resins to give the corresponding resin-supported ruthenium vinylcarbene catalysts **PS-1**, **PS-3** and **PS-4**, presumably attached to the resin through bis-phosphine linkages. This assignment was made on basis of the similarities between the  $^{31}\text{P}$  NMR chemical shifts of the PS–DVB-supported catalysts and their homogeneous counterparts.

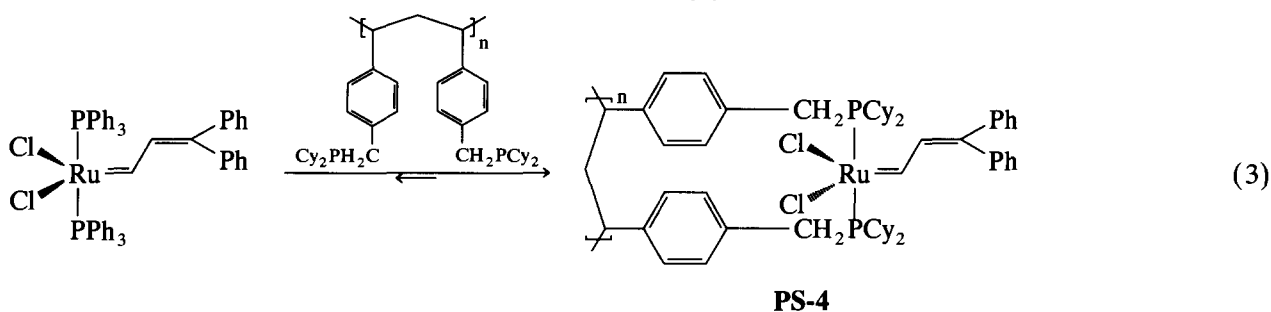
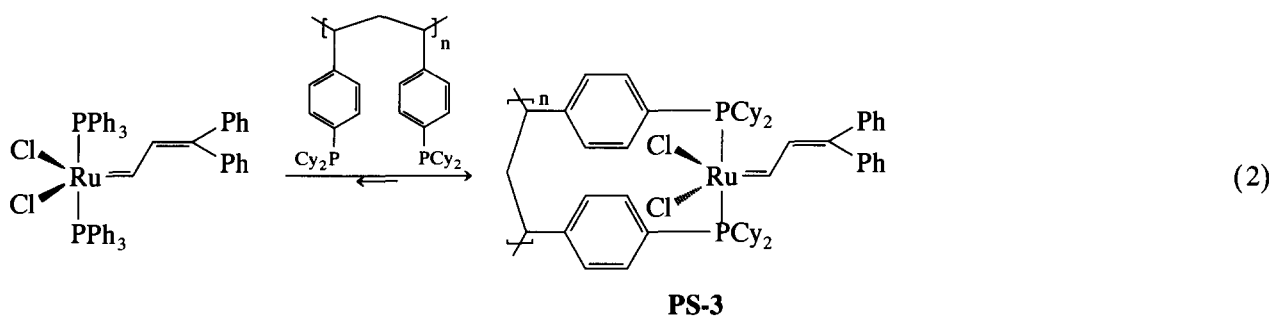
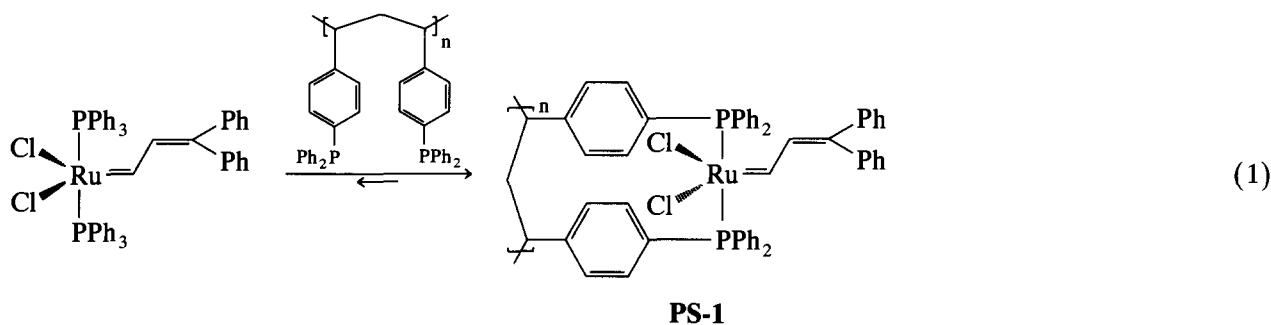
### 2.2. The activities and recyclability of polystyrene–divinylbenzene-supported ruthenium carbene olefin metathesis catalysts

Similar to their homogeneous analogs, catalysts **PS-1**, **PS-3** and **PS-4** exhibit metathesis activities correspond-

ing to the nature of the PS-linked phosphines. For example while **PS-1** catalyzes the ROMP of the highly strained norbornene, it does not metathesize acyclic olefin such as *cis*-2-pentene. On the contrary, **PS-3** and **PS-4** will catalyze both the metathesis of *cis*-2-pentene and the ROMP of less strained cyclic olefins such as cyclooctene. The more electron-rich catalyst **PS-4** metathesizes *cis*-2-pentene with a turn-over number (TON) of  $2\text{ h}^{-1}$ . The TON for the metathesis of *cis*-2-pentene in  $\text{C}_6\text{D}_6$  by **PS-3** ( $0.1\text{ h}^{-1}$ ) is slower than that of **PS-4** and is about 150 times slower than that of its homogeneous analog  $\text{Cl}_2(\text{PPhCy}_2)_2\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$  (**3**) [18]. This retardation in rate may be attributed to three reasons.

(1) Incomplete substitution of phosphine: since the phosphine exchange reaction is governed by an equilibrium and mixed-phosphine species  $\text{Cl}_2(\text{PR}_3)(\text{PPh}_3)\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$  can be observed in the homogeneous exchange between  $\text{PR}_3$  and  $\text{Cl}_2(\text{PPh}_3)_2\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$  [18]; a large percentage of the total ruthenium complexes on the resin can potentially be mixed-phosphine species, which are very slow acyclic olefin metathesis catalysts.

(2) Diffusion limit on metathesis rate: in contrast with the homogeneous metathesis reaction where both the catalyst and the olefin are dispersed throughout the solution, the heterogeneous olefin metathesis reaction as



catalyzed by these PS–DVB-supported catalysts is limited by the diffusion of the olefin into the cavities of the crosslinked PS–DVB support. This diffusion limitation had been observed in PS–DVB-supported rhodium(I) hydrogenation catalysts [19].

(3) Phosphine chelation effect: if the main mechanism for the metathesis reaction is of a dissociative nature (i.e. going through a 14-electron  $\text{Cl}_2(\text{PR}_3)\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$  intermediate), then the presence of a local high concentration of phosphine such as that on the support will slow down the metathesis rate. Indeed, there is accumulated evidence to support the dissociative pathway for the olefin metathesis reaction catalyzed by **2** [8,20]. The chelation also drastically increases the cross-link density in the local environment of the catalyst center.

The decrease in general acyclic metathesis rates of these PS–DVB-supported catalysts is offset by the extended lifetime of the supported catalysts and our ability to recycle and re-use the solid-phase ruthenium vinylcarbene. A common decomposition mode of carbene-based olefin metathesis catalysts is of a bimolecular mechanism where two carbenes combined to yield an olefin and two unreactive metal center. Thus spacing the catalyst molecules on the polystyrene support as reported herein should eliminate this decomposition pathway and enhance the lifetime of the catalyst. We have cycled catalyst **PS-4** through three complete metathesis of *cis*-2-pentene (100 equivalents each) in  $\text{C}_6\text{D}_6$  over a period of 30 days with a small loss of activity (20% after each cycle). This experiment demonstrated that the PS-supported ruthenium carbene catalyst are long lived and can be re-used in practical circumstances.

For all polymerizations using these PS–DVB-supported catalysts, the polydispersity index (PDI) of the polymer products tends to be much higher than normally achieved with the homogeneous analog. For example, the ROMP of norbornene as catalyzed by **1** routinely gives polymers with PDI ranging 1.1 to 1.3 [16] while the ROMP of norbornene catalyzed by **PS-1** yields a polymer with a PDI of 5.5. Again, this phenomena can be attributed to both multiple-site and diffusion limitation problems.

### 3. Conclusion

This first generation of PS–DVB-supported ruthenium vinylcarbene metathesis catalyst represents the first time that a well-defined organometallic metathesis catalyst is attached to a polymeric support. This approach offers the promise that given the right conditions these PS–DVB-supported catalysts can be used in a manner analogous to solid-phase peptide synthesis to generate several libraries of monodispersed ROMP-type

block copolymers. Additionally, the polymer back-biting problem such as in the case of homogeneous ROMP chemistry might be minimized by the sterically constrained nature of the cross-linked PS–DVB support and the synthesis of ROMP polymers with new stereochemical composition (e.g. high *cis* backbone) might be realized.

Although initial experiments with the first generation of PS–DVB-supported ruthenium metathesis catalysts have suggested that, in contrast with Merrifield resin chemistry where only one peptide link is formed at each reaction site during a single coupling, the ROMP chemistry using these PS–DVB-supported ruthenium carbene catalysts is less selective in the sense that different numbers of links can be formed at different reaction sites depending on the time scale of the reaction and the location of the site. In addition, the slow initiation rate of the vinylcarbene catalyst can further contribute to the broad molecular weight distribution problem. Both of these problems can be avoided by using a different carbene complex and resins with a lower DVB cross-linked density. These will be the subjects of a future report.

## 4. Experimental details

### 4.1. General considerations

All manipulations were performed using standard Schlenk techniques or dry-box procedures. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Solid organometallic compounds were transferred and stored in a nitrogen-filled Vacuum Atmospheres dry-box.  $^{31}\text{P}$  NMR spectra were recorded with a JEOL FX-90Q ( $^1\text{H}$ , 89.60 MHz;  $^{13}\text{C}$ , 22.53 MHz,  $^{31}\text{P}$ , 36.2 MHz) spectrometer (locking on a static  $^7\text{Li}$  lock sample and with reference to an external 85%  $\text{H}_3\text{PO}_4$  sample where a 10 mM solution of  $\text{PPh}_3$  in  $\text{CDCl}_3$  exhibits a resonance at  $-5.4$  ppm).  $^1\text{H}$  NMR spectra were recorded with a QE-300 Plus ( $^1\text{H}$ , 300.10 MHz) spectrometer. NMR data are reported as follows: chemical shifts (multiplicity (br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), integration, assignment and coupling constant).  $^1\text{H}$  NMR chemical shifts are reported downfield from tetramethylsilane (TMS) ( $\delta$  scale) with TMS employed as the internal standard.  $^{31}\text{P}$  NMR spectra of the benzene-swollen PS–DVB-supported catalysts were carried out in a non-spinning mode with a 3 Hz line broadening applied during the processing of the FID. In general, the  $^{31}\text{P}$  resonances of the polymeric catalysts measured in this manner are consistently broad owing to the restricted mobility of the  $^{31}\text{P}$  nuclei and the chemical shifts positions are

about  $\pm 3$  ppm different from that of a homogeneous sample.

#### 4.2. Materials

Methylene chloride, methylene chloride- $d_2$ , and  $N,N,N',N'$ -tetramethylene ethylenediamine (TMEDA) were dried over  $\text{CaH}_2$ , vacuum transferred and then degassed by three continuous freeze–pump–thaw cycles. Pentane was stirred over concentrated  $\text{H}_2\text{SO}_4$ , dried over  $\text{MgSO}_4$  and  $\text{CaH}_2$  and then further dried over sodium-benzophenone ketyl solubilized with tetraglyme. Tetrahydrofuran (THF), benzene and benzene- $d_6$  were dried over sodium-benzophenone ketyl and vacuum transferred into a storage flask.  $\text{CIPCy}_2$  was obtained from Strem Chemical Company and was used as received.  $\text{LiPCy}_2$  was collected as a pale-yellow solid from the reaction of  $n\text{-BuLi}$  in hexane (obtained from Aldrich) and  $\text{HPCy}_2$  (obtained from Strem Chemical Company).  $(\text{Ph}_3\text{P})_2\text{Cl}_2\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$  (**1**) [5] was synthesized according to literature procedures.

Triphenylphosphine-functionalized polystyrene ( $\text{PS-PPh}_2$ ) resin (2% cross-linked  $\text{PS-DVB}$ ; 200–400 mesh; 3 mmol  $\text{P}(\text{g resin})^{-1}$ ) was obtained from Fluka (catalogue No. 93093), chloromethylated polystyrene ( $\text{PS-}p\text{-CH}_2\text{Cl}$ ) resin (2% cross-linked  $\text{PS-DVB}$ ; 200–400 mesh; 0.43 mequivalents of  $\text{Cl}$  ( $\text{g of resin})^{-1}$ ) was obtained from Polyscience (catalogue No. 09011) and used as received. To obtain maximum *para* substitution, lithiated polystyrene ( $\text{PS-Li}$ ) resin (2% cross-linked  $\text{PS-DVB}$ ; 25–60 mesh) is synthesized from brominated polystyrene ( $\text{PS-Br}$ ) (which in turns is prepared from purified polystyrene [21] obtained as a gift from Dow Chemical Company) according to a procedure described by Farral and Frechet [21]. *cis*-Cyclooctene (95%) and *cis*-2-pentene were obtained from Aldrich, distilled over  $\text{CaH}_2$  and degassed through three freeze–pump–thaw cycles. Norbornene was obtained from Aldrich, dried over sodium benzophenone ketyl, vacuum transferred into a flask equipped with a Kontes 4 mm Teflon valve and stored at  $-30^\circ\text{C}$  before use.

For the polymer work-up, 2,6-di-*tert*-butyl-4-methylphenol (BHT) and ethyl vinyl ether were obtained from Aldrich;  $\text{CH}_2\text{Cl}_2$  and methanol were obtained from EM Science and used as received.

#### 4.3. The synthesis of $(\text{PS-PPh}_2)_2\text{Cl}_2\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$ (**PS-1**)

In the dry-box, **1** (200 mg, 0.225 mmol) and  $\text{PS-PPh}_2$  resin (250 mg; fluka catalogue No. 93093; 2% crosslinked  $\text{PS-DVB}$ ; 200–400 mesh, 3 mmol  $\text{P}(\text{g resin})^{-1}$ ) were weighed into a 50 ml Schlenk flask equipped with a magnetic stir bar.  $\text{CH}_2\text{Cl}_2$  (25 ml) was then added and the mixture was stirred at room temperature for 40 h during which time the amber beads turned

deep green. The supernatant was filtered away and the remaining beads were washed with benzene ( $3 \times 25$  ml with 30 min stirring during each wash) and  $\text{CH}_2\text{Cl}_2$  ( $3 \times 25$  ml with 30 min stirring during each wash). The remaining resin beads were then dried under vacuum overnight.

$^{31}\text{P}$  NMR (benzene-swollen sample of the catalyst):  $\delta$   $-5$  (br, residual  $\text{PS-PPh}_2$ ), 30 (br, **PS-1**) ppm.  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$  solution of  $(\text{PPh}_3)_2\text{Cl}_2\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$ ):  $\delta$  28.2 (s) ppm.

$^{31}\text{P}$  NMR (benzene-swollen sample of  $\text{PS-PPh}_2$  resin):  $\delta$   $-8.4$  (br, Fluka  $\text{PS-PPh}_2$  resin) ppm.  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$  solution of  $\text{PPh}_3$ ):  $\delta$   $-5.4$  (s) ppm.

The combined filtrate was dried in vacuo to a greenish-white powder mixture (100 mg) and analyzed by  $^{31}\text{P}$  NMR to show a 4:1 composition of  $\text{PPh}_3$ : **1** which corresponded to a total of 54 mg  $\text{PPh}_3$  released and 46 mg of **1** remained. On the basis of this result, an estimated catalyst loading of  $0.57 \text{ mmol (Ru)(g of resin)}^{-1}$  was calculated.

#### 4.4. The synthesis of $(\text{PS-}p\text{-PCy}_2)_2$ resin

In the dry-box,  $\text{PS-Li}$  freshly prepared from  $\text{PS-Br}$  (2 g; 2% cross-linked  $\text{PS-DVB}$ ; 25–60 mesh; 1 mequivalent  $\text{Br}(\text{g resin})^{-1}$ ) was suspended in THF (25 ml) in a 100 ml Schlenk flask equipped with a magnetic stir bar.  $\text{CIPCy}_2$  (470 mg, 1.01 equivalents) was then added dropwise to the reaction mixture over 5 min during which time the deep-red color of the resin faded. The mixture was stirred at room temperature for 1 h more. The supernatant was filtered away and the beads were washed with THF ( $3 \times 20$  ml with 30 min stirring during each wash). The remaining light-amber–orange resin beads were then dried under vacuum overnight.

$^{31}\text{P}$  NMR (benzene-swollen sample of  $\text{PS-}p\text{-PCy}_2$  resin):  $\delta$  0.7 (br) ppm.  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$  solution of  $\text{PPhCy}_2$ ):  $\delta$  2.5 (s) ppm.

#### 4.5. The synthesis of $(\text{PS-}p\text{-PCy}_2)_2\text{Cl}_2\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$ (**PS-3**)

In the dry-box, the  $\text{PS-}p\text{-PCy}_2$  resin prepared above (1.5 g) was swollen for 30 min in benzene (20 ml) in a 50 ml Schlenk flask equipped with a magnetic stir bar. A solution of **1** (650 mg, 0.731 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) was then added and the mixture was stirred at room temperature for 40 h during which time the beads turned deep red and the green solution became much lighter in color. The supernatant was filtered away and the remaining beads were washed with benzene ( $3 \times 25$  ml with 30 min stirring during each wash) and  $\text{CH}_2\text{Cl}_2$  ( $3 \times 25$  ml with 30 min stirring during each wash). The remaining beads were then dried under vacuum overnight.

$^{31}\text{P}$  NMR (benzene-swollen sample of the catalyst):  $\delta$  –0.4 (br, residual PS-*p*-PCy<sub>2</sub>), 41.7 (br, **PS-3**) ppm.  $^{31}\text{P}$  NMR (C<sub>6</sub>D<sub>6</sub> solution of (PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>Ru=CH–CH=CPh<sub>2</sub>):  $\delta$  44.8 (s) ppm.

The combined filtrate was dried in vacuo to a greenish-white powder mixture (450 mg) and analyzed by  $^{31}\text{P}$  NMR to show a 1:1 composition of PPh<sub>3</sub>: **1** which corresponds with a total of 167 mg PPh<sub>3</sub> released and 283 mg of **1** remained. On the basis of this result, an estimated catalyst loading of 0.22 mmol (Ru)(g resin)<sup>–1</sup> was calculated.

#### 4.6. The synthesis of (PS-*p*-CH<sub>2</sub>PCy<sub>2</sub>) resin

In the drybox, the PS-*p*-CH<sub>2</sub>Cl resin (1 g; Polyscience catalogue No. 09011; 2% cross-linked PS–DVB; 200–400 mesh; 0.43 mequivalent Cl(g resin)<sup>–1</sup>) was slurried in THF (20 ml) in a 50 ml Schlenk flask equipped with a magnetic stir bar. LiPCy<sub>2</sub> (89 mg; 1.01 equivalents) was then added as a solid followed by TMEDA (1 ml). The reaction mixture was then taken out of the dry-box, attached to a reflux condenser and refluxed for 40 h. The supernatant was filtered away and the beads were washed with THF (3 × 20 ml with 30 min stirring during each wash). The remaining pale-yellow resin beads were then dried under vacuum overnight.

$^{31}\text{P}$  NMR (benzene-swollen sample of PS-*p*-CH<sub>2</sub>PCy<sub>2</sub> resin):  $\delta$  0.7 (br) ppm.  $^{31}\text{P}$  NMR (C<sub>6</sub>D<sub>6</sub> solution of PPhCy<sub>2</sub>):  $\delta$  2.5 (s) ppm.

#### 4.7. The synthesis of (PS-*p*-CH<sub>2</sub>PCy<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>Ru=CH–CH=CPh<sub>2</sub> (**PS-4**)

In the dry-box, the PS-*p*-CH<sub>2</sub>PCy<sub>2</sub> resin prepared above (1 g) was swollen for 30 min in benzene (20 ml) in a 50 ml Schlenk flask equipped with a magnetic stir bar. A solution of **1** (160 mg, 0.18 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) was then added and the mixture was stirred at room temperature for 40 h during which time the beads turned dark orange–yellow and the green solution became much lighter in color. The supernatant was filtered away and the remaining beads were washed with benzene (3 × 25 ml with 30 min stirring during each wash). The remaining beads were then dried under vacuum overnight.

$^{31}\text{P}$  NMR (benzene-swollen sample of the catalyst):  $\delta$  33.2 (br, **PS-4**) ppm.

The combined filtrate was dried in vacuo to a greenish-white powder mixture (110 mg) and analyzed by  $^{31}\text{P}$  NMR to show a 1:1 composition of PPh<sub>3</sub>: **1** which corresponds to a total of 41 mg of PPh<sub>3</sub> released and 69 mg of **1** remained. On the basis of this result, an estimated catalyst loading of 0.1 mmol (Ru)(g resin)<sup>–1</sup> was calculated.

#### 4.8. Monitoring the acyclic olefin metathesis activities of polystyrene–divinylbenzene-supported catalysts

In a typical experiment, the resin **PS-3** and **PS-4** ( $5 \times 10^{-3}$  mmol of Ru) were weighted into a Teflon-lined screw-cap 5 mm NMR tube inside the dry-box. C<sub>6</sub>D<sub>6</sub> (0.6 ml) was then added followed by *cis*-2-pentene (42 mg, 100 equivalents). The tube was then sealed, taken out of the box and attached to a rotor to ensure complete mixing. The reaction content was then monitored periodically by  $^1\text{H}$  NMR.

#### 4.9. Experiments on the recycling and re-use of catalyst **PS-4**

After the content of a *cis*-2-pentene metathesis reaction has reached equilibrium, the NMR tube was taken back into the dry-box. The liquid phase was drained off using a glass wool-packed pipet and the remaining beads were washed with C<sub>6</sub>D<sub>6</sub> (2 × 0.6 ml). A fresh sample of C<sub>6</sub>D<sub>6</sub> (0.6 ml) was then added followed by another aliquot of *cis*-2-pentene (42 mg, 100 equivalents). The tube was again sealed, taken out of the box and attached to a rotor to ensure complete mixing. The reaction content was then monitored periodically by  $^1\text{H}$  NMR.

#### 4.10. Polymerization of norbornene catalyzed by **PS-1**

In a typical experiment, the resin **PS-1** (0.005 mmol) was swollen in C<sub>6</sub>H<sub>6</sub> (0.5 ml) in a 10 ml vial equipped with a magnetic stir bar inside the dry-box. Norbornene (70.62 mg, 150 equivalents) in C<sub>6</sub>H<sub>6</sub> (2.5 ml) was next added to the catalyst mixture. The vial was capped and allowed to stirred for 5 h inside the dry-box during which time the mixture became viscous.

The work-up was as follows. The reaction vial was taken out of the dry-box and to it was added a solution consisting of CH<sub>2</sub>Cl<sub>2</sub> (2 ml), ethyl vinyl ether (0.1 ml) and BHT (10 mg). This mixture was then stirred at room temperature for 2 h. This solution was then removed using a glass wool-packed pipet and precipitated into a vigorously stirred methanol solution (40 ml, containing 0.1% BHT). The resulting polymer was then washed with methanol (5 ml, containing 0.1% BHT) and dried under vacuum overnight (yield, 61 mg (87.8%) of a white solid), GPC (vs. polystyrene standard):  $M_w$  = 98.900 K; PDI, 5.5.

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