Transfer of the Fluorous Biphasic Concept to the Palladium-Catalyzed Addition Polymerization of Norbornene

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Two perfluorinated palladium(II) pre-catalysts of the type $(Ar^F_3P)_2PdCl_2$ ($Ar^F = m$-C_8F_{17}-C_2H_4-C_6H_4- and p-C_7F_{15}-CH_2-O-C_6H_4-) could be highly activated with the co-catalyst $B(C_6F_5)_3$/$AlEt_3$ or methylalumoxane (MAO) for the vinyl/addition polymerization of norbornene. Their recycling was studied by using the FBS concept (*Fluorous Biphasic System*).

*Key words:* Polymerization, Norbornene, Fluorous Biphasic System, Palladium

Introduction

The use of expensive catalysts or pre-catalysts in combination with co-catalysts requires the search for economical, ecological, and selective methods including possibilities to recover and recycle the applied catalysts. A simple and efficient separation of product and catalyst is an important prerequisite for a successful homogeneous catalysis in industrial processes [1]. A very elegant approach to this requirement is the use of liquid-liquid biphasic systems in homogenous catalysis [2], for example the aqueous biphasic system in the Ruhrchemie/Rhône-Poulenc-Process [3], the catalytical reaction in supercritical CO_2 [4,5], catalysis in molten salts [6,7] and the use of a phase-separation and immobilization technique known as FBS (*Fluorous Biphasic System*) [8–12].

The FBS concept, developed by Horvath and Rabai [9], uses a perfluorinated liquid and an organic solvent. Perfluorocarbons are usually immiscible or poorly miscible with organic solvents at room temperature and under atmospheric pressure so that a biphasic system can be obtained. With perfluorinated ligands the catalyst is tailored to be preferably soluble in the perfluorinated phase and, thus, segregated from reagents and products before and after the catalytic process. Upon increasing temperature and/or pressure the miscibility of the perfluorinated and the organic phase can be increased strongly and the possibility to work under homogeneous conditions becomes available. The return to the starting temperature or pressure

conditions results again in the formation of a biphasic system – the perfluorinated and the organic phase – and gives the possibility of an easy and effective separation and recycling of the catalyst. Thus, a FBS system can combine the advantages of homogeneous reaction with the biphasic product separation by running the reaction at higher temperatures and separating the product or recycling the catalysts at lower temperatures. In addition to this the FBS concept is accepted as an ecologically sensitive method. Also, perfluorinated solvents have the advantage that they are neither flammable nor toxic and recoverable by simple distillation [13–15].

The FBS concept has been successfully applied to a multitude of catalytic reactions like the hydrofomylation [9,16] and hydroboration of alkenes [17,18], the oxidation of aldehydes [19], thioethers [19], and alkanes [20], the Wacker oxidation of alkenes [21], epoxidation [19,22–25], Rh-catalyzed carbenoid-reaction [26], palladium-mediated allylic alkylation [27], palladium-catalyzed cross-coupling of organozinc bromides with aryl iodides [28], the Heck-reaction [29], the Stille-coupling [30], and the Suzuki-coupling [31]. The oligomerization of ethylene with nickel-catalysts is also possible under FBS conditions [32].

Since we are interested in the vinyl/addition polymerization of norbornene we would like to describe in this paper the first investigation to transfer the FBS concept to the field of polymerization. The homopolymerization of norbornene can be accomplished by three different routes with each route leading to its
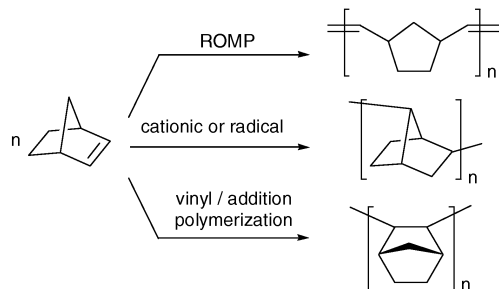
Scheme 1.

own polymer type with different structure and properties (Scheme 1).

Polymers produced via ring-opening-metathesis-polymerization (ROMP) still contain double bonds in the polymer backbone and can be obtained by a number of transition metals in high oxidation state [33]. Only a few reports describe the formation of low molar mass oligomeric material with 2,7-connectivity of the monomer from the cationic or radical homopolymerization of norbornene [34]. Finally, the vinyl or addition polymerization of norbornene yields saturated 2,3-inserted rotationally constrained polymers in which the bicyclic structural unit remains intact and only the double bond of the π-component was opened. Catalysts containing the metals titanium, zirconium, chromium, and currently the late transition-metals cobalt, nickel and palladium are described in the literature for the vinyl/addition polymerization of norbornene [35 – 37]. The late transition-metal complexes are commonly activated with methylalumoxane (MAO), except for the cationic palladium-complexes $[Pd(NCR)_4]^{2+}2A^-$ (NCR weakly bound nitrile-ligand; A = "non"-coordinating counter ion). Another co-catalytic system for the activation of metal complexes is the organo-Lewis acid tris(pentafluorophenyl)borane, $B(C_6F_5)_3$ with or without triethylaluminum (AlEt$_3$). This co-catalytic system is known from the activation process of transition-metal group 4 metallocene catalysts in olefin polymerization [38] and was recently

also applied to the activation of late transition-metal complexes for the (co)polymerization of cyclopentene [39], ethene [40], norbornene and norbornene derivatives [36b, 37b, 41, 42].

The homopolymer vinyl-poly(norbornene) is of interest as a specialty polymer with good mechanical strength, heat resistance, and optical transparency, e.g. for deep ultraviolet photoresists, interlevel dielectrics in microelectronics applications or as cover layer for liquid-crystal displays [35, 43].

Here, we describe the use of the palladium(II) pre-catalysts bis(tri-3-(1H,1H,2H,2H-heptadecafluoro-decyl)phenylphosphine)palladium(II)dichloride (**1**) and bis(tri-4-(1H,1H-pentadecafluoroctyloxy)phenyl-phosphine)palladium(II)dichloride (**2**) in combination with the co-catalysts methylalumoxane (MAO) and tris(pentafluorophenyl)borane, $B(C_6F_5)_3$/triethylaluminum (AlEt$_3$) in the vinyl/addition polymerization of norbornene by using the FBS concept (Scheme 2).

Results and Discussion

The transfer of the FBS concept to the vinyl polymerization of norbornene by using the new, perfluorinated palladium(II) pre-catalysts **1** and **2** should allow for the chemical recovery of the active species by working in a biphasic system. Separation of the fluorous phase containing the perfluorinated (active) metal species should open the possibility to restart the polymerization by a simple addition of a new portion of monomer. Multinuclear NMR studies provided strong evidence that the phosphine ligand remains bound to the metal and that the initial activation with $B(C_6F_5)_3$/AlEt$_3$ proceeds through a halide abstraction [36c]. FC72 (perfluorohexane, mixture of isomers) was used as the perfluorinated solvent and *n*-hexane was selected as the solvent of the organic phase. FC72 and *n*-hexane are completely miscible at room temperature and the possibility to work under homogeneous conditions becomes available without heating the polymerization mixture. The required
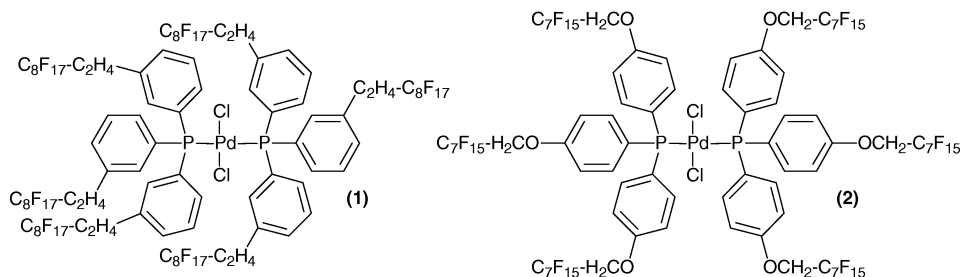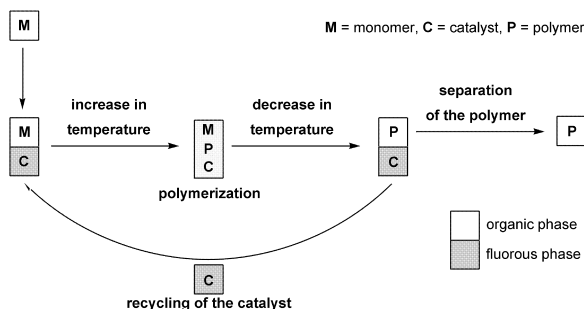

Scheme 2.

Fig. 1. Schematic representation of the vinyl polymerization of norbornene using the FBS concept (*Fluorous Biphasic System*).
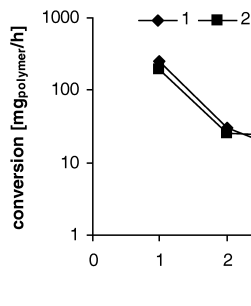

Fig. 2. Polymerization behaviour of the palladium(II) pre-catalysts **1** and **2** under FBS conditions and in combination with $B(C_6F_5)_3/AlEt_3$ as co-catalytic system. The following molar ratios of the compounds were applied in the first run: Pd:norbornene = 1:2000, Pd:$B(C_6F_5)_3$:AlEt$_3$ = 1:9:10. Detailed conditions are given in the Experimental Section.

formation of the biphasic system (before and) after the polymerization of norbornene can be achieved by cooling the mixture to 0 °C [44]. The main principles of the polymerization procedure are schematically represented in Fig. 1.

No polymerization activity could be observed by simple overlayering and mixing of the fluorous phase containing the palladium pre-catalysts **1** or **2** with the monomer solution. Addition of the co-catalyst $B(C_6F_5)_3/AlEt_3$ or MAO was necessary to induce polymerization activity [36, 41]. The vinyl polymerization of norbornene was carried out by using the perfluorinated palladium(II) pre-catalysts **1** and **2** in combination with the co-catalytic systems $B(C_6F_5)_3/AlEt_3$ or MAO. The polymerization results are graphically depicted in Fig. 2 and Fig. 3. Because of the unknown amount of the recycled active species the activity results are represented in [mg$_{polymer}$/h] instead of [g$_{polymer}$/mol$_{metal}$·h].

In the first run the polymerization activities of the perfluorinated palladium complexes with $B(C_6F_5)_3/AlEt_3$ of $1.64 \cdot 10^5$ g$_{polymer}$/mol$_{Pd}$·h for **1** and $1.28 \cdot 10^5$ g$_{polymer}$/mol$_{Pd}$·h for **2** surpass those of most other diphosphine-palladium dichloride complexes [36c,d]. The monomer conversion of 86% and 68% for **1** and **2**/$B(C_6F_5)_3/AlEt_3$, respectively, is remarkable. Yet, in both cases the conversion of norbornene dropped significantly after the first polymerization run and continued to decrease, albeit less so, in the following four catalytic cycles (Fig. 2). The smaller conversions in the polymerization runs 2 to 5 might be explained by the partial separation and recycling of the active species as a result of the formation of a biphasic system. However, without the addition of fresh $B(C_6F_5)_3/AlEt_3$ co-catalyst no activity could be
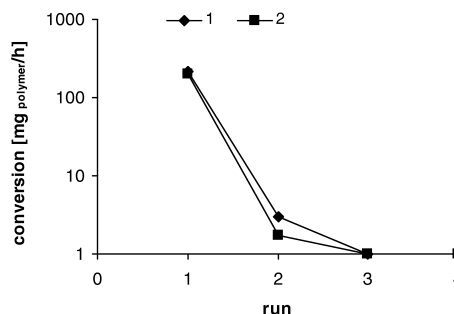

Fig. 3. Polymerization behaviour of the palladium(II) pre-catalysts **1** and **2** under FBS conditions and in combination with methylaluminoxane (MAO) as co-catalyst. The following molar ratios of the compounds were applied in the first run: Pd:norbornene = 1:2000, Pd:Al = 1:100. Detailed conditions are given in the Experimental Section.

observed. The necessary addition of $B(C_6F_5)_3/AlEt_3$ before each run more likely suggests that the continued polymerization is achieved through activation of newly and perhaps first-time activated pre-catalyst molecules in the fluorous phase. Previous studies have demonstrated that only a fraction of the nickel or palladium pre-catalysts becomes activated by $B(C_6F_5)_3/AlEt_3$ or MAO [36, 41]. After the phase separation not-activated pre-catalyst molecules should be held in the fluorous phase and be available for subsequent activation. Use of the MAO co-catalyst gave polymerization activities of $1.45 \cdot 10^5$ g$_{polymer}$/mol$_{Pd}$·h for **1** (77% monomer conversion) and $1.36 \cdot 10^5$ g$_{polymer}$/mol$_{Pd}$·h for **2** (72% monomer conversion) in the first run. Again, it was necessary to add the co-catalyst before the next cat-
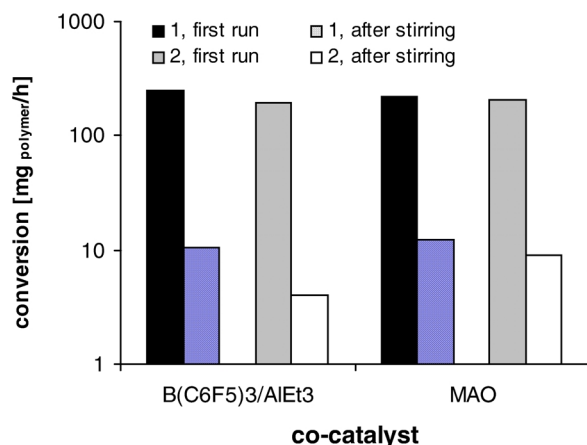
Fig. 4. Results of the attempt to transfer the polymer-incorporated catalyst species from the polymer to the fluorous solvent. The separated polymer of the first polymerization run was stirred for several hours in the perfluorinated solvent FC72. The fluorous phase with newly-added co-catalyst was subsequently applied in the polymerization process.

alytic cycle but the monomer conversion became insignificant after the first polymerization run. In contrast to an activation with $B(C_6F_5)_3$/AlEt$_3$ only traces of polymer were found after the second polymerization run with **1** or **2**/MAO and no activity was observed in the fourth run (Fig. 3).

The significant drop of the monomer conversion after the first polymerization run using $B(C_6F_5)_3$/AlEt$_3$ or MAO as co-catalyst can be explained by the incorporation of the active species in the growing polymer chain resulting in an immobilization of the catalyst. For this reason, no recovery of the active species could be achieved after the separation of the fluorous and the organic phase. In an attempt to recycle the polymer-incorporated catalyst species, the polymers of the first polymerization runs were stirred for several hours in the perfluorinated solvent FC72. Even through this route the transfer of the catalyst from the polymer into the fluorous solvent FC72 was not very successful. Monomer conversions in the subsequent polymerization runs with addition of new co-catalyst were only between 2% and 6% of conversions achieved in the first polymerization run (Fig. 4).

Perfluorinated palladium(II) pre-catalysts of the type $(Ar^F_3P)_2PdCl_2$ proved to by highly active with the co-catalyst $B(C_6F_5)_3$/AlEt$_3$ or methylalumoxane (MAO) for the vinyl/addition polymerization of nor-

bornene. However, the aim to recycle the active species by working in a fluorous biphasic system was not achieved in the vinyl polymerization of norbornene with these perfluorinated palladium (pre-) catalysts. After each recycling step the addition of new $B(C_6F_5)_3$/AlEt$_3$ or MAO co-catalyst became necessary and monomer conversions dropped considerably after the first recycling. The low recovery rate of the catalyst can be explained by inclusion and immobilization of the active species in the growing polymer chain. The FBS concept may more advantageously be applied in polymerizations where a soluble polymer is initially obtained. Still, the activation of new pre-catalyst molecules after phase separation allowed for a more economic use of the metal complexes where only a fraction is activated in each cycle.

Experimental Section

General procedures

All work involving air- and/or moisture-sensitive compounds was carried out by using standard vacuum, Schlenk or drybox techniques with argon 5.0 (99.999% purity) as inert gas. FT-IR spectra (KBr pellet) were measured on a Bruker Optik IFS 25.

Materials

FC72 (Fluka), hexafluorobenzene (Aldrich), methylalumoxane (10 wt.-% solution in toluene, Witco), tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, (Aldrich), and triethylaluminum (AlEt$_3$, 1 mol/l solution in hexane, Merck-Schuchardt) were used as received. *n*-Hexane was dried over sodium metal, distilled and stored under nitrogen. Methylene chloride was dried over CaH$_2$. Norbornene (bicyclo[2.2.1]hept-2-ene, Aldrich) was purified by distillation and used as a solution in toluene. Bis(tri-3-(1H,1H,2H,2H-heptadecafluorodecyl)phenyphosphine)palladium(II)dichloride (**1**) [31] and bis(tri-4-(1H,1H-pentadecafluoroctyloxy)phenylphosphine)-palladium(II)dichloride (**2**) [45] were synthesized by literature procedures.

Polymerization procedures

Under inert gas a 25 ml Schlenk-tube was charged with the pre-catalyst ($1.5 \cdot 10^{-3}$ mmol) in hexafluorobenzene (1.0 ml) and methylene chloride (1.0 ml). FC72 (3 ml) and $B(C_6F_5)_3$ ($1.35 \cdot 10^{-2}$ mmol) in FC72 (2.0 ml) was added and the mixture was cooled in an ice bath. After layering this mixture with norbornene (3.0 ml) dissolved in *n*-hexane (1.0 ml) and a solution of AlEt$_3$ ($1.5 \cdot 10^{-2}$ mmol) in *n*-hexane (0.15 ml) the ice bath was removed and the mixture was stirred for 1 h. A homogeneous phase was observed after 5 min. The polymerization was stopped after 1 h by cooling

the mixture with an ice-bath and the biphasic system was formed again. The fluorous phase was removed by syringe and placed in another argon-filled and ice-cooled Schlenk-tube. Before starting the second polymerization run the volume of the fluorous phase was reduced *in vacuo* to a volume of about 3 ml before adding $B(C_6F_5)_3$ ($1.35 \cdot 10^{-2}$ mmol) in FC72 (2.0 ml) and layering the fluorous phase with the norbornene and $AlEt_3$ solutions as described above. Workup of the polymer proceeded by stirring for 30 min in a 10:1 methanol/conc. HCl mixture, filtering and drying *in vacuo* for 3 h.

When using MAO instead of $B(C_6F_5)_3/AlEt_3$ the co-catalyst MAO (0.15 mmol) in toluene (0.1 ml) was added after the addition of norbornene. The polymerization was then carried out as described above.

The IR spectra of the poly(norbornene)s obtained with the catalysts **1** and **2** showed the absence of double bond bands at 1620 cm^{-1} to 1680 cm^{-1}. This ensured the vinyl/addition polymerization instead of a ring-opening metathesis polymerization (ROMP). The conversion was calculated by gravimetric analysis of the polymer.

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