Poly(2-oxazoline)s Functionalized with Palladium Carbene Complexes: Soluble, Amphiphilic Polymer Supports for C–C Coupling Reactions in Water

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ABSTRACT: This paper describes the synthesis and characterization of a new class of amphiphilic, water-soluble diblock copolymers based on 2-oxazoline derivatives with pendent N-heterocyclic carbene/palladium catalysts in the hydrophobic block. The synthetic strategy involves a four-step synthesis of three functionalized monomers, each composed of a bis(imidazoline-2-ylidene)palladium(II) diiodide derivative that is covalently linked to a 2-oxazoline monomer via a flexible alkyl spacer (alkyl = butyl, hexyl, octyl). The structure of the monomers was analyzed by 1H and 13C NMR spectroscopy, MALDI-TOF, and elemental analysis. Three diblock copolymers P1–P3 with the monomers being part of the hydrophobic block were prepared by living cationic ring-opening polymerization. The structure and composition of the polymers was characterized by 1H and 13C NMR spectroscopy as well as GPC measurements and indicated rather low PDI of 1.3 and about 65% incorporation of the N-heterocyclic carbene/palladium-functionalized monomer into the polymer. Dynamic light scattering measurements of the polymers P1–P3 in water revealed aggregate formation with a hydrodynamic radius of 10–30 nm with high polydispersity as visualized by TEM micrographs. Subsequently, polymers P1–P3 were successfully utilized as a polymeric support for the Heck coupling of iodobenzene with styrene as a model reaction in water, showing high activities with turnover frequencies (TOF) up to 570 h⁻¹ at 90 °C.

Introduction

Soluble and insoluble polymer supports have received much interest recently in combinatorial chemistry and catalysis. This is not surprising considering the industrial need for highly efficient transformation of any given substrate and the economic benefits of recyclable catalyst systems for long-term usage. Whereas homogeneous catalysis offers the advantages of simplified product purification and the potential for catalyst recycling. In addition, replacement of expensive, toxic, and flammable organic solvents by water is highly desirable for reducing costs and development of environmentally benign processes. Due to the rapid developments in aqueous-phase catalysis, the need for organometallic catalysts that are stable and active in aqueous media has been a major driving force for the intensive research activity in this field over the last 15 years. In the past decade metal complexes of N-heterocyclic carbenes (NHC) have been reported as a class of moisture- and air-stable catalysts with remarkable activity in various C–C coupling reactions. The stronger metal–carbon bond of these ligands compared to the conventional phosphine ligands reduces the dissociation from the metal center even at elevated temperatures, making the thermally and oxidatively stable NHC complexes useful catalysts for Heck and Suzuki coupling reactions in both organic and aqueous media as well.

Recently, an increasing number of research groups have focused on the development of new support materials for catalysis in water based on poly(ethylene glycol), poly(acrylic acid), or poly(N-isopropylacrylamide) copolymers. However, transformation of hydrophobic substrates in pure aqueous media without the use of any organic cosolvent still remains a challenging task due to their limited water solubility. The most promising approach to increase the solubility of hydrophobic substrates in aqueous media is based on the use of amphiphilic polymer supports. Of particular interest is the work of Uozumi et al., who utilized commercially available poly(ethylene glycol)-modified polystyrene resins for catalyst immobilization in various transition-metal-catalyzed reactions in pure aqueous media. More recently, Yamada et al. described the preparation of a heterogeneous palladium catalyst by supramolecular self-assembling of (NH3)2PdCl4 and poly[(N-isopropylacrylamide)10-co-(4-diphenylstyrylphosphine)]. However, typical limitations of cross-linked polymer materials, such as lowered reactivity and extended reaction times, remain unsolved. In addition, fine tuning of the structure and composition of the polymer support to allow a better correlation with catalyst activity is an important feature of any support material and difficult to achieve for heterogeneous catalyst supports.

The scope of this contribution is the preparation of three soluble, amphiphilic block copolymers with palladium N-heterocyclic carbene catalysts in the hydrophobic block by using appropriate functionalized monomers. First, results of these polymer-bound catalysts in a micellar catalytic variant of the Heck reaction of iodobenzene with styrene in water revealed TOF numbers up to 570 h⁻¹, which are the highest ever reported
for this reaction in neat water without addition of any organic cosolvent.

Results and Discussion

1. Monomer Synthesis. The cationic ring-opening polymerization of 2-oxazolines provides a versatile monomer system for the synthesis of amphiphilic polymers with different architecture, composition, and functionalization. Two different approaches can be utilized to incorporate the catalytically active unit into the polymer: either (i) directly via suitable functionalized monomers or (ii) in a polymer analogous modification step. As a result of the well-known drawbacks of the second approach, such as low degree of polymer modification and separation of the polymer from unreacted compounds, the first strategy seems to be the most elegant and reliable methodology.

Due to the fact that oxazolines are well known to be excellent ligands for metal catalysts, our first objective was to explore the influence of the NHC/palladium catalyst on the polymerization behavior of 2-oxazoline, whether the catalyst disturbs the living cationic polymerization or not. Two test experiments were conducted using 2-methyl-2-oxazoline as monomer and bis(1,3-dimethylimidazol-2-ylidene)palladium(II) diiodide as the NHC/palladium catalyst (Scheme 1).

Thus, a homopolymer of 2-methyl-2-oxazoline was prepared with a monomer/initiator ratio ([monomer]:[initiator]) = 15. In the first experiment the polymerization was initiated with methyl triflate at 0 °C; after 12 h the reaction was terminated with piperidine. The polymer was precipitated in diethyl ether, and the catalyst was isolated after evaporation of diethyl ether. The polymer and catalyst were characterized by 1H NMR spectroscopy. The degree of polymerization was calculated based on 1H NMR end-group analysis and gave a value of 23 (theoretical 15), indicating clearly that the palladium catalyst disturbs the living cationic polymerization mechanism. 1H NMR of the catalyst showed methylation of the N-heterocyclic carbene ligands by methyl triflate. As a consequence, in the second experiment we used 2,3-dimethyl-2-oxazolinium triflate as initiator salt, which was obtained after reacting 2-methyl-2-oxazoline with 1 equiv of methyl triflate according to a literature procedure. 1H NMR end-group analysis revealed excellent agreement of the theoretical and experimental degree of polymerization. NMR analysis of the NHC/palladium catalyst after polymerization did not show any changes in the structure of the catalyst.

On the basis of these preliminary results, the monomer route was chosen to introduce the catalytically active NHC/palladium complex in the polymer. We decided to attach the catalyst to the 2-oxazoline unit via a flexible alkyl spacer, where we anticipated that the linker would place the catalyst sufficiently away from the polymer backbone to allow unimpeded access of the substrate to the metal center. The synthetic scheme depicted in Scheme 2 was chosen as the most direct route to functionalized monomers with the NHC/palladium catalyst attached to the 2-oxazoline monomer unit via the alkyl spacer of four, six, or eight methylene units.

Purification of each step was achieved by column chromatography. The soluble intermediates were readily characterized by 1H and 13C NMR spectroscopy. In addition, the color change of the catalyst with each derivatization step provided a qualitative means of the success of each reaction. The first step in the synthesis involved the alkylation of N-methylimidazole with 1,ω-dibromoalkane to give the imidazolium salts 1a–c in yields of 68–73% as colorless oils. Low amounts of disubstituted 1,ω-dibromoalkanes were removed by column chromatography. The imidazolium salts 1a–c were then subjected to the same synthetic protocol as that previously described for the preparation of mixed NHC/phosphine palladium complexes. Therefore, compounds 1a–c were treated with palladium(II) acetate in the presence of sodium iodide and KOtBu in THF and resulted in orange-colored dimeric products 2a–c. In dichloromethane and THF these complexes show a deep red color, which is typical for such dinuclear complexes. Additional, successful halogen exchange by the Finkelstein reaction due to an excess amount of sodium iodide was monitored by 1H NMR spectroscopy, showing a new signal at 3.25 ppm. According to NMR analysis, at least 80% of the bromide was replaced by iodide, which is of advantage for coupling to the 2-methyl-2-oxazoline in the last step of monomer synthesis due to the higher reactivity of the iodide. Moreover, successful complex formation was confirmed by shifting of the aromatic signals for the protons from 7.78 and 7.71 ppm to 7.40 and 7.41 ppm, respectively. At room temperature the mixed complexes 3a–c were prepared from THF solutions of 2a–c by addition of 1 equiv of 1,3-dimethylimidazol-2-ylidene that was prepared according to a literature procedure and were obtained as yellow solids. 13C NMR spectroscopic analysis of 3a clearly showed successful formation of the mixed complex by the appearance of a second signal at 121.9 ppm, which corresponds to the carbon atom close to the N-alkyl group, meNCHCHNalk in addition to the signal at 122.9 ppm that can be assigned to the three other carbon atoms meNCHCHNalk and meNCHCHNme. 1H NMR analysis shows two signals at 7.31 ppm which can be assigned to meNCHCHNalk and a second signal at 7.28 ppm corresponding to meNCHCHNme and meNCHCHNalk with an intensity ratio of 1:3.

Synthesis of the functional monomers was accomplished by treating a solution of 2-methyl-2-oxazoline deprotonated with lithium diisopropylamide (LDA) in THF at −60 °C with the intermediate compounds 3a–c for 2 h. The pure monomers 4a–c were obtained after column chromatography as pale yellow compounds. The structure and composition of 4a–c were confirmed by 1H and 13C NMR spectroscopy, MALDI-TOF, and elemental analysis. Figure 1 shows the 1H NMR spectrum of 4c. Characteristic are the two methylene groups of the oxazoline ring at 3.66 (−N−CH2−) and 4.12 ppm
Figure 1. 1H NMR spectrum of monomer 4c (d6-DMSO, 300.1 MHz, T = 20 °C).

Scheme 2. Synthetic Scheme for the Functionalized 2-Oxazoline Monomers 4a–c

(-O-CH2-) – The singlets at 7.26 and 7.28 ppm can be clearly assigned to the protons of the imidazoline ring.

2. Synthesis of the Polymeric Macroligand. As already shown, the living chain end of the poly(2-oxazoline)s does not interfere with the N-heterocyclic carbene functionalities of monomers 4a–c. Thus, diblock copolymers were prepared by sequential polymerization of 2-methyl-2-oxazoline to form the hydrophilic block, which provides water solubility, and subsequently a mixture of monomer 4a–c with the corresponding 2-alkyl-2-oxazoline was used to form the second block. 2-Alkyl-2-oxazolines with alkyl = butyl, hexyl, octyl side chains were hereby added to increase the hydrophobicity of the second polymer block. The synthesis is depicted in Scheme 3.

Piperidine was used as a highly effective termination agent. After polymerization was finished, the polymers were precipitated several times in diethyl ether and obtained as citrus-colored solids. The results of the polymer synthesis are summarized in Table 1. Size exclusion chromatography gave monomodal curves with polydispersity indices ranging from 1.32 to 1.39.

1H NMR analysis indicated successful polymerization of the NHC/palladium catalyst carrying monomers. Quantitative analysis of polymer composition and palladium content as determined by 1H NMR spectroscopy and ICP–OES revealed roughly 65% incorporation of the functional monomers 4a–c into the polymer. Two reasons might account for this result. Since it has already been demonstrated that 2-oxazoline polymerization is not hindered by the NHC/palladium catalyst, it can be speculated that the sterically more demanding NHC/palladium catalyst in the monomer side chain is the reason for the lowered reactivity of the monomers. The 1H NMR spectrum of P3 is depicted in Figure 2. The signal at 3.43 ppm can be clearly assigned to the polymer main chain protons. In addition, the signals at 3.90 and 6.85 ppm can be assigned to the three methyl groups and the ring protons of the NHC/palladium catalyst, respectively.

3. Dynamic Light Scattering (DLS) and TEM Analysis. The study of aggregate formation was guided by two considerations. First, we wanted to make sure that micellar aggregates were formed at the polymer concentrations used in the catalytic experiments. In addition, we were interested in finding out if there is any correlation between aggregate size and catalytic activity. Aggregate formation of P1–P3 in water was analyzed by DLS measurements at a similar polymer concentration used in the later catalysis reactions. The results are summarized in Table 2. The hydrodynamic radii of the particles were in the range of 10–30 nm, which is typical for micellar aggregates based on poly(2-oxazoline)s with a similar molar mass and block copolymer composition.

It is interesting to note, however, that there is no direct correlation of spacer length of the side chain and the hydrodynamic radii of the aggregates formed.

TEM micrographs of the aggregates formed by P1 confirmed the high polydispersity of the aggregates with an average hydrodynamic radius of about 15 nm (see Figure 3). This result has been found more recently also for other poly(2-oxazoline) block copolymers. However, as reported by Papadakis and co-worker, understanding the aggregate formation of such amphiphilic block copolymers with a comblike structure in the hydrophobic block is very complex and still at an early stage.

4. Heck Reaction in Aqueous Media. Heck coupling of sp2-halides with alkenes promoted by palladium catalysts is one of the most important methods for C–C coupling in organic synthesis, the synthesis of important intermediates for pharmaceuticals, and conducting polymers. Although many efforts have been made to prepare heterogeneous Heck catalysts, homogeneous catalysts still have many advantages on catalytic activity. A major problem of the immobilized catalysts is their reduced stability under Heck reaction conditions. Moreover, salts accumulated during the reaction lead to degradation of the catalytic system.

Few reports have been presented so far that deal with Heck coupling in water without use of any organic cosolvents. Jeffery intensively studied the reaction of iodobenzene with methyl acrylate in the presence of Pd(OAc)2/PPh3 in pure aqueous solution and the beneficial effect of various tetrabutylammonium halides. Another typical test reaction is the coupling of styrene as a more hydrophobic substrate with iodobenzene to give trans-stilbene. The first approach to react iodobenzene derivatives and various olefinic substrates under Heck conditions in water was presented by Y. Uozumi et al. They used a PS–PEG resin-supported palladium catalyst and obtained 92% yield after 14 h reaction time of styrene with iodobenzene in pure aqueous solution.
with 10 mol % palladium catalyst showing excellent recyclability but poor activities (TOF < 1 h⁻¹).⁷a

We tested macroligands P1–P3 in a micellar catalytic variant of the Heck reaction of iodobenzene with styrene. Reactions were conducted at 90 °C with P3 and a palladium content of 0.67 mol %. The course of the reaction was monitored by periodically taking samples and analyzing them by gas chromatography. Figure 4 shows the kinetics of substrate conversion and product formation. As can be seen from Figure 4 there is an induction period of 15 min to form the catalytically active species by reducing palladium(II) to palladium(0) with K₂CO₃ as the base. After 3 h reaction time 93% of trans-stilbene as well as 4% of 1,1-diphenylethene and less than 0.5% of cis-stilbene as side products were detected. The reaction is very fast, and almost 90% of all substrates are already converted after 40 min. The

Table 1. Analytical Data of the Amphphilic Polymer Supports P1–P3

<table>
<thead>
<tr>
<th>polymer</th>
<th>xexp/calcd</th>
<th>yexp/calcd</th>
<th>zexp/calcd</th>
<th>Mₙ, NMR</th>
<th>Mₚ, NMR</th>
<th>PDI, x</th>
<th>γ/%, y</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>28.4 (30.7)</td>
<td>1.5 (2.4)</td>
<td>2.9 (3.0)</td>
<td>3920 (2584)</td>
<td>1.32 (1.35)</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td>29.9 (32.2)</td>
<td>1.8 (2.7)</td>
<td>3.2 (3.2)</td>
<td>4400 (2661)</td>
<td>1.35 (1.33)</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td>30.4 (30.6)</td>
<td>1.9 (2.9)</td>
<td>3.4 (3.1)</td>
<td>4730 (2668)</td>
<td>1.39 (1.32)</td>
<td>3.6</td>
<td></td>
</tr>
</tbody>
</table>

Variation in the content of x, y, and z, see Scheme 3.

We tested macroligands P1–P3 in a micellar catalytic variant of the Heck reaction of iodobenzene with styrene. Reactions were conducted at 90 °C with P3 and a palladium content of 0.67 mol %. The course of the reaction was monitored by periodically taking samples and analyzing them by gas chromatography. Figure 4 shows the kinetics of substrate conversion and product formation. As can be seen from Figure 4 there is an induction period of 15 min to form the catalytically active species by reducing palladium(II) to palladium(0) with K₂CO₃ as the base. After 3 h reaction time 93% of trans-stilbene as well as 4% of 1,1-diphenylethene and less than 0.5% of cis-stilbene as side products were detected. The reaction is very fast, and almost 90% of all substrates are already converted after 40 min. The
the spacer length of four methylene units is too short to separate the catalyst sufficiently from the polymer backbone. According to our results a minimum spacer length of six methylene groups is needed to achieve an optimal combination of catalyst flexibility and the possibility of being accessed by the substrates. Comparing the catalytic results of P1 to P3 with the size of the aggregates as determined by dynamic light scattering, the results show clearly that there is no correlation of aggregate size and catalytic activity; rather the spacer length between the polymer backbone and the catalytically active unit are crucial parameters for optimal catalyst activity. However, it should also be noted that the results obtained by DLS at room temperature cannot be transferred directly to the reaction conditions at $T = 90 \, ^\circ\text{C}$.

5. Catalyst Recycling and Reuse. After the reaction was complete, the product could be easily separated by extraction with diethyl ether. The recovered aqueous phase containing the catalyst was reused in another reaction cycle. By doing so, two more cycles have been performed to demonstrate separation and reuse of the polymer-bound catalyst P3. The results summarized in Table 4 show a slightly reduced activity in the second cycle and reduced trans-stilbene formation of 6%. In the third cycle product formation was again reduced by 9% with respect to the second cycle. This is however due to incomplete phase separation more than catalyst deactivation, which is known to show thermal stability up to 140 °C. Moreover, we assume that after extraction with diethyl ether a considerable amount of solvent stays solubilized in the micellar core that prevents efficient solubilization of the substrate again and is in addition responsible for the reduced activity in the second cycle. In a more detailed study, however, leaching experiments should be performed to rule out any catalyst decomposition. New developments in catalyst separation, such as nanofiltration, are particularly interesting for such soluble support systems due to the higher molecular weight of the polymer-bound ligand, have already been proven to be very useful in catalyst recycling without any loss of activity in a second or third cycle, and will help to overcome this problem in future experiments.

In summary, we presented the first synthesis of amphiphilic, water-soluble block copolymers based on 2-oxazolines with pendant NHC/palladium catalysts. The polymeric catalysts P1–P3 reveal aggregate formation in water with a hydrodynamic radius of 10–30 nm. Using the polymer-bound catalysts P1–P3 in the Heck coupling of iodobenzene and styrene as a model reaction gave TOF values of up to 570 h$^{-1}$, which are the highest ever reported for this reaction in neat water without use of any organic cosolvent. In view of the promising results, it is expected that the synthetic approach provides a versatile approach for the synthesis of other NHC/palladium-functionalized polymers. More detailed

**Figure 4.** Kinetics of the Heck coupling of iodobenzene (PhI) and styrene as a function of amphiphile P1–P3 at $T = 90 \, ^\circ\text{C}$ (PhI:styrene:K$_2$CO$_3$ = 1.0:1.25:1.5, $n_{PhI}/n_{PhI} = 0.0067$).

**Figure 5.** Reaction kinetics of the Heck coupling of iodobenzene (PhI) at 90 °C (PhI:styrene:K$_2$CO$_3$ = 1.0:1.25:1.5, $n_{PhI}/n_{PhI} = 0.0067$).

**Table 3.** Catalytic Results of the Heck Coupling of Iodobenzene (PhI) with Styrene with the Polymer-Bound Catalysts P1–P3 (PhI:styrene:K$_2$CO$_3$ = 1.0:1.25:1.5, $c_p = 0.67 \, \text{mM}, n_{PhI}/n_{PhI} = 0.0067$).

<table>
<thead>
<tr>
<th>polymer</th>
<th>$t$ (h)$^a$</th>
<th>trans-stilbene (%)$^b$</th>
<th>TOF (h$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>P1</td>
<td>2</td>
<td>&gt;93</td>
<td>150</td>
</tr>
<tr>
<td>P2</td>
<td>1.5</td>
<td>&gt;93</td>
<td>570</td>
</tr>
<tr>
<td>P3</td>
<td>1.5</td>
<td>&gt;93</td>
<td>530</td>
</tr>
</tbody>
</table>

$^a$ Reaction time. $^b$ trans-Stilbene as determined by gas chromatography.

**Table 4.** Catalytic Results of the Heck Coupling of Iodobenzene (PhI) with Styrene with the Polymer-Bound Catalysts P3 (PhI:styrene:K$_2$CO$_3$ = 1.0:1.25:1.5, $c_p = 0.17 \, \text{mM}, n_{PhI}/n_{PhI} = 0.1 \, \text{mol \%}, T = 90 \, ^\circ\text{C}$).

<table>
<thead>
<tr>
<th>cycle</th>
<th>$t$ (h)$^a$</th>
<th>conversion (%)</th>
<th>trans-stilbene (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>89</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>82</td>
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</tr>
<tr>
<td>3</td>
<td>5</td>
<td>76</td>
<td>68</td>
</tr>
</tbody>
</table>

$^a$ Reaction time. $^b$ trans-Stilbene as determined by gas chromatography.
studies on the catalytic performance of the macroligands P1–P3 in Heck and Suzuki coupling with various substrates are currently under investigation.

**Experimental Section**

**Acronyms.** alkyl (alk), broad (br), 2-butyl-2-oxazoline (butox), carbene (car), degree of polymerization (Pd), 2-hexyl-2-oxazoline (hexox), imidazolium (im), mass % (m%, melting point (mp), methyl (me), 2-methyl-2-oxazoline (metox), 2-octyl-2-oxazoline (octox), oxazoline (ox), piperidine (pip), polydispersity index (PDI), refractive index (RI), retention factor (r).

**Measurements.** H NMR (300.13 MHz) and 13C NMR (75.47 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. FT-IR spectroscopy was carried out on a Bruker IFS 55 spectrometer. Elemental analyses were determined by the Microanalytical Laboratory of the Institute of Technology, TU München. Size exclusion chromatography (SEC) was carried out on a Waters GPC 510 equipped with UV and RI detectors using poly(styrene) calibration for the poly(2-oxazoline) samples in chloroform as solvent. MALDI-TOF measurements were performed on a Bruker Biflex III using chloroform as solvent and 1,8,9-trihydroxyanthracline (dithranol) as matrix substance. UV–vis spectra were recorded on a Varian Cary 3 spectrometer. A John Yvon JY 38 plus was used for ICP–OES measurements, a MLS 1200 mega for microwave experiments. Gas chromatographic analyses were performed on a Varian CP-3380, capillary column CP– Sil 8 CB, length 25 m, with helium in combination with a flame ionization detector. 1H and 13C NMR (300.13 MHz, 20 °C): 12 was filtered through silica using ethyl acetate as solvent to give 3.52 (t, 3 JH2C2Br), 2.72 (s, 3H; C3), 3.07 (t, 3J = 6.9 Hz, 2H; im-CH2), 3.10 (t, 3J = 6.9 Hz, 2H; im-CH2), 3.50 (t, 3J = 6.7 Hz, 2H; CH2Br), 3.85 (s, 3H; CH3), 4.15 (t, 3J = 7.1 Hz, 2H; im-CH2), 7.15 (s, 1H, 1H=NCH=CH=), 7.75 (s, 1H, 1H-NCH=CH=). 13C NMR (300.13 MHz, 20 °C): 128.4 (d, CH2), 28.3 (CH2), 29.5 (im-CH3), 32.3 (CHBr), 35.4 (CH2CHBr), 36.0 (CH3), 48.9 (im-CH3), 122.4 (m-NCH=CH=), 123.8 (m-NCH=CH=), 136.7 (NCH). IR (ATR, substance): 130.6 (cm–1) = 3056 m (v C=C), 2928 vs (v C=C), 2854 s (v C=C), 1630 w (v C=C), 1570 s (v C=C), 1467 s (v C=N), 1459 m (δ CH2, δ CH2), 1430 m (δ CH2, δ CH2), 1378 w (δ CH2, 1248 m (δ CH2, δ CH2), 1165 vs (δ C–C), 1092 w, 1020 w, 870 m, 824 m, 752 m, 725 w (γ CH2), 648 s, 620 vs.

**Synthesis of the Dinuclear Palladium Complexes (a–c).** The imidazolium salt (a–c, 23.3 mmol, 1 equiv), palladium acetate (5.00 g, 23.3 mmol, 1 equiv), KOBu (2.50 g, 22.3 mmol, 1 equiv), and sodium iodide (26.7 g, 178 mmol, 8 equiv) were stirred in 500 mL of THF at room temperature overnight. After rotary evaporation of THF, the dark residue was precipitated by column chromatography (SiO2, ethyl acetate: hexane = 1:1).

**Di-N-iodobuty-1-(4'-iodobutyl)-3-methylimidazolide-2-ylidene dipalladium(II) Diiodide (2a).** Yield 8.98 g (7.2 mmol, 65%), orange-colored solid, mp = 164.5 °C (± 1.0 °C), r = 0.56. 1H NMR (300.13 MHz, 20 °C): δ = 1.80 (tt, 3J = 6.8 Hz, 3J = 7.0 Hz, 2H; im-CH2), 2.04 (tt, 3J = 6.9 Hz, 3J = 6.9 Hz, 4H; CH2C=CH1), 2.38 (t, 3J = 6.9 Hz, 4H; CH2), 3.73 (s, 6H; CH3), 4.19 (t, 3J = 7.0 Hz, 4H; im-CH2), 7.42 (s, 4H; NCH=CH=). 13C NMR (300.13 MHz, 20 °C): δ = 7.6 (CH2), 29.8 (CH2CH3), 30.2 (im-CH2CH3), 38.6 (CH3), 49.5 (im-CH2C=CH1), 123.0 (m-NCH=CH=), 124.4 (m-NCH=CH=), carbene signal not detected. IR (ATR, substance): 130.6 (cm–1) = 3122 m (ν C=C), 3031 w (ν C=C), 2937 s (ν C=C), 2856 m (ν C=C), 1653 m (ν C=C), 1569 m (ν C=C), 1467 s (ν C=C), 1418 m (δ CH2, δ CH2), 1386 w (δ CH2, δ CH2), 1301 m, 1285 s, 1204 m, 1170 m, 1117 m, 1094 m, 1014 w, 728 m (γ CH2, 1269 m), 698 vs.

**Di-N-iodobuty-1-(4'-iodobutyl)-3-methylimidazolide-2-ylidene dipalladium(II) Diiodide (2b).** Yield 8.39 g (6.4 mmol, 58%), orange-colored, orange-colored solid, mp = 144.2 °C (± 1.0 °C), r = 0.64. 1H NMR (300.13 MHz, 20 °C): δ = 1.36 (m, 8H; CH2), 1.77 (tt, 3J = 7.3 Hz, 3J = 6.8 Hz, 4H; CH2C=CH1), 1.99 (tt, 3J = 7.3 Hz, 3J = 6.8 Hz, 4H; im-CH2), 3.26 (t, 3J = 7.2 Hz, 4H; CHJ1), 3.73 (s, 6H; CH3), 4.15 (t, 3J = 7.3 Hz, 4H; im-CH2), 7.41 (s, 2H, m-NCH=CH=), 7.42 (s, 2H, m-NCH=CH=). 13C NMR (300.13 MHz, 20 °C): δ = 9.0 (C1), 25.0 (CH2), 28.6 (CH2), 29.5 (CH2), 38.5 (CH3), 48.5 (im-CH2), 122.0 (m-NCH=CH=), 123.0 (m-NCH=CH=), carbene signal not detected. IR (ATR, substance): 130.6 (cm–1) = 3124 w (ν C=C), 3033 vw (ν C=C), 2930 s (ν C=C), 2855 m (ν C=C), 1653 m (ν C=C), 1569 m (ν C=C), 1471 s (δ CH2, δ CH2), 1418 s (δ CH2, δ CH2), 1243 s (m-NCH=CH=).
CH₂, δ(CH₂), 1368 w (δ(CH₂), 1262 m, 1222 m, 1193 m, 1166 w, 1124 w, 1083 m, 1016 m, 803 m, 730 vs (γ(CH₂), CH₃)), 670 vs.

Di-α-iodobutyl-1,8-octadecyl-3-methylimidazoline-2-ylidene-dipalladium(II) Diiodide (2e). Yield 9.45 g (6.9 mmol, 82%).

\[ \text{CH₂}, \delta(CH₂), 1368 w (\delta(CH₂), 1262 m, 1222 m, 1193 m, 1166 w, 1124 w, 1083 m, 1016 m, 803 m, 730 vs (\gamma(CH₂), CH₃)), 670 vs.} \]

Synthesis of the Mononuclear Palladium Complexes (3a–e). In a glovebox the dinuclear complex (2a–c, 5 mmol, 1 equiv) was dissolved in 250 mL of THF and stirred at room temperature. Then 0.96 g (10 mmol, 2 equiv) of 1,3-dimethylimidazolyl iodide 50 mL of THF was added dropwise within 1 h. Stirring was continued for a further 30 min. After rotary evaporation of the solvent, the yellow residue was purified by column chromatography (SiO₂, ethyl acetate: hexane = 1:1).

[1-(4′-Iodomethyl)-3-methylimidazoline-2-ylidene]1,3-dimethylimidazoline-2-ylidene]dipalladium(II) Diiodide (3a). Yield 6.9 g (5.8 mmol, 58%).

\[ \text{[1-(4′-Iodomethyl)-3-methylimidazoline-2-ylidene]1,3-dimethylimidazoline-2-ylidene]dipalladium(II) Diiodide (3a). Yield 6.9 g (5.8 mmol, 58%).} \]

Monomer 4a. Yield 1.40 g (2.1 mmol, 52%), pale yellow-colored solid, \( r_1 = 0.24 \).

Synthesis of the Complex Functionalized 2-Oxazoline Monomers (4a–e). A portion of 2.5 mL of LDA (2 m solution in hexane, 5.0 mmol, 1.25 equiv) and 10 mL of THF were placed in a 50 mL flask equipped with a 20 mL addition funnel. To the solution, was added dropwise under N₂. The resulting mixture was stirred for 2 h at –60 °C. Then 4.0 g (1 equiv) of the precursor (3a–e) dissolved in a mixture of 6 mL of THF and 6 mL of hexamethylphosphoric acid triamide (HMPT) was added dropwise within 20 min at –78 °C. The mixture was warmed to –50 °C and stirred for a further 2 h. After the solution was warmed to room temperature over the next 30 min, was separated by rotary evaporation. The residue was purified by column chromatography (SiO₂, ethyl acetate: NEt₃ = 15:1) and freeze-dried benzene.

[1-(6-Iodoethyl)-3-methylimidazoline-2-ylidene]1,3,3-di-
methylimidazoline-2-ylidene]dipalladium(II) Diiodide (3b). Yield 5.20 g (4.7 mmol, 71%).

\[ \text{[1-(6-Iodoethyl)-3-methylimidazoline-2-ylidene]1,3,3-di-
methylimidazoline-2-ylidene]dipalladium(II) Diiodide (3b). Yield 5.20 g (4.7 mmol, 71%).} \]

Monomer 4b. Yield 1.54 g (2.2 mmol, 55%), pale yellow-colored solid, \( r_1 = 0.31 \).
4.43; I, 35.96; N, 9.92; Pd, 15.08. Found: C, 32.62; H, 4.68; I, 35.04; N, 10.02; Pd, 15.44.

**Monomer 4c.** Yield 1.36 g (19 mmol, 46%), pale yellow-colored solid, r1 = 0.40. [1H NMR (d2-DMso, 300.13 MHz, 20 °C): δ = 1.25 (t, J = 7 Hz, H2 CH3); 1.31 (t, J = 7 Hz, H2 CH3); 1.50 (m, 2H, CH2CH3O); 1.99 (m, 2H, im-CH2CH3); 2.16 (t, J = 7.4 Hz, 2H, CH2-ox); 3.66 (t, J = 9.4 Hz, 2H, -NCH2-); 3.78 (s, 6H, CH2OH); 3.83 (s, 3H, alk-C); 4.12 (t, J = 7.4 Hz, 2H, OCH2-); 4.22 (1H, d, J = 7.5 Hz, 2H, im-CH2); 7.26 (s, 3H, -NCH=CH-NW), -NCH=CH-NW), 7.28 (s, 1H, -NCH=CH-CO)1.31] [13C NMR (d2-DMso, 75.47 MHz, 20 °C): δ = 25.6 (CH3), 26.3 (CH3), 27.3 (CH3), 28.7 (CH3), 28.8 (CH2), 29.0 (CH2), 28.9 (CH2), 37.4 (CH3), 37.6 (CH3), 37.8 (CH3), 50.2 (im-CH2), 54.0 (-NCH2), 66.7 (OCH3), 121.9 (-NCH=CH-NW), 122.9 (-NCH=CH-NW), -NCH=CH-NW), 166.7, 166.8, 169.9 (-NCH=CH-NW), -NCH=CH-NW), OCN). IR (ATR, sublimed): v(CO) = 2138 cm-1, v(C = O) = 1760 cm-1, v(C=N) = 1434 cm-1, v(N=O) = 1349 cm-1. Synthesis of the Polymers (P1–P3). In a polymerization vessel 1 equiv of methyl triflate was dissolved in tetrachloroethane so that the final concentration of methyl triflate is about 30–40 mm. To this solution 3 equiv of 2-methyl-2-oxazoline was added at room temperature. The reaction mixture was stirred at 80 °C for 12 h. At room temperature the metal-complex-functionalized monomer (4a–c, 2 equiv) as well as the corresponding unfunctionalized 2-alkyl-2-oxazoline (2 equiv) were added. The clear solution was stirred at 60 °C for an additional 24 h. At room temperature 1.25 equiv of piperidine was added as terminating reagent, and the mixture was stirred for 3 h. Afterward 3 equiv of fine-ground potassium carbonate was added, and the suspension was stirred for 4 h. After filtration, the polymer was purified by reprecipitation (diethyl ether) and dialysis using a membrane (molar mass cutoff at 1000 g mol-1) and tetrachloroethane as solvent to remove the low molecular weight byproducts, which are soluble in diethyl ether.

**P1.** Yield 0.59 g (83%), citrus-colored solid. P1 (determined by 1H NMR end-group analysis): (metox)2n[(4a), 5b] (metox)2n] (Mn = 3920 g mol-1). SEC (CHCl3, RI, poly(styrene) calibration): hydrophilic block Mw = 1380 g mol-1, Mw = 1870 g mol-1, PD1 = 1.35; block copolymer Mw = 2410 g mol-1, Mw = 3190 g mol-1, PD1 = 1.32. ICP–OES (Pd): 3.3% mol.Pd(4a) = 1.2. [1H NMR (CDCl3, 300.13 MHz, 20 °C): δ = 0.88 (t, J = 6.1 Hz, -CH2CH3); 1.32 (sbr, CH2); 1.51 (sbr, CH2); 1.54 (sbr, -C=OCH2); 1.76 (sbr, -C=OCH2); 1.90 (sbr, -C=OCH2); 2.05, 2.08, 2.11 (s, s, s; -C=OCH2); 2.30 (sbr, -C=OCH2), 2.32 (sbr, -C=OCH2), 2.92 (s; CH2-end group, ZCH3-CO), 3.02 (s; CH2-end group, E3H31-CO), 3.43 (sbr, CH2-backbone), 3.91 (sbr, car-CH2), 4.29 (t, J = 7.0 Hz, car-CH2), 6.85 (sbr, NCH=CH). 13C NMR (CDCl3, 75.47 MHz, 20 °C), signal groups: δ = 14.1 (hexox-CH3), 21.1 (metox-COCH3), 22.6 (CH3), 25.2–25.5 (CH3), 26.8 (CH3), 29.1–29.5 (CH3), 31.8 (COCH2-CH2), 38.2–38.5 (car-CH2), 43.4–43.9 (CH2-backbone), 44.8–45.7 (CH2-backbone), 46.3–47.2 (CH2-backbone), 47.5–48.1 (CH2-backbone), 51.1–51.3 (car-CH2), 122.2–122.5 (NCH=CH-NW), 170.6–171.5 (CO=O), UV–vis (H2O, c = 0.2 g L-1, d = 1 cm): block copolymer λ (in cm2 mg-1) = 200–244 (>20 000; polymer), 262 (17 400; car), 302 (16 300; PdI), 330s (7300) to 410s (700), 460–900 (<300); hydrophilic block λ (in cm2 mg-1) = 200–226 (>20 000; polymer), 262 (1300), 300 (700), 380–900 (<300).

**ICP–OES Measurements.** Aqua regia (3.0 mL) was added to the supported catalyst (10.0 mg). The mixture was placed inside high-pressure Teflon tubes, and leaching was carried out under microwave conditions (5 min, 600, and 450 W pulses, respectively, t = 32 min). After cooling to room temperature, the mixture was filtered and measured by ICP–OES for Pd (λ = 340.658 nm, atom line). The background was measured at λ = 340.416 and 340.4997 nm.

**Micellar Catalysis.** Catalysis Experiments. All catalysis experiments were carried out under argon in 50 mL reaction tubes. In 10 mL of degassed water a portion of the polymer (P1–P3) was dissolved so that the concentration of the polymer is about 0.1–0.9 mm. Iodobenzene, potassium carbonate as base, and tetradecont as internal standard were added (iodobenzene:styrene:K2CO3 = 1:25:1.5). The mixture was stirred and heated to the respective reaction temperature. Then catalysis was started by adding styrene. The course of the reaction was monitored by periodically taking samples and analyzing them by means of gas-chromatographic analysis.

**Recycling Experiments.** After a reaction time of 5 h, the reaction vessel was cooled to room temperature using an ice/ water cooling bath. Afterward a portion of 10 mL of degassed diethyl ether was added. For extraction of the products and potential residues of the starting compounds, the vessel was agitated for 15 min. After a waiting period of at least 2 h, nearly complete phase separation occurs. Then the organic phase was removed using a syringe and analyzed by gas chromatography. The remaining aqueous phase is still catalytically active and was reused for the next runs in the same manner as that described above.

**References and Notes**

(1) For reviews, see: (a) Kollhofer, A.; Plenio, H. Chem Eur J. 2003, 9 (6), 1416. (b) Osburn, P. L.; Bergbreiter, D. E. Prog.


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