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 ^{1}H and ^{13}C 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 ^{1}H and ^{13}C 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.[1] 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 often provides the best conditions to achieve high activities, heterogeneous 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.[2] Due to the rapid developments in aqueous two-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.[3] 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.[4] 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 candidates for Heck and Suzuki coupling reactions in both organic and aqueous media as well.[5]

Recently, an increasing number of research groups have focused on the development of new support materials for catalysis in water based on poly(ethylene glyocle),[6] poly(acrylic acid),[7] or poly(*N*-isopropylacrylamide) copolymers.[8] 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.[3e] Of particular interest is the work of Uozumi et al., who utilized commercially available poly(ethylene glycole)-modified polystyrene resins for catalyst immobilization in various transition-metal-catalyzed reactions in pure aqueous media.[9] More recently, Yamada et al. described the preparation of a heterogeneous palladium catalyst by supramolecular self-assembling of $(NH_4)_2PdCl_4$ and poly[(*N*-isopropylacrylamide)$_{10}$-*co*-(4-diphenylstyrylphosphine)].[10] 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

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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.[11] 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.

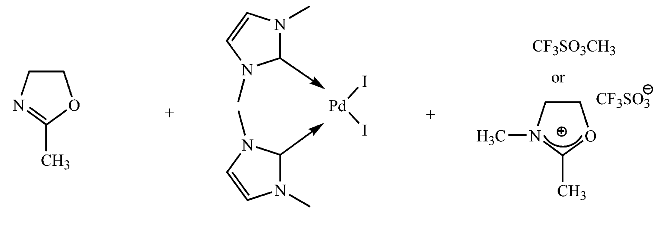
Due to the fact that oxazolines are well known to be excellent ligands for metal catalysts,[12] our first objective was to explore the influence of the NHC/palladium catalyst on the polymerization behavior of 2-oxazoline, whether the catalyst disturbs the living cationic polymerization or not. Two test experiments were conducted using 2-methyl-2-oxazoline as monomer and bis(1,3-dimethylimidazoline-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. Polymer and catalyst were characterized by ^{1}H NMR spectroscopy. The degree of polymerization was calculated based on ^{1}H NMR end-group analysis and gave a value of 23 (theoretical 15), indicating clearly that the palladium catalyst disturbs the cationic ring-opening polymerization mechanism. ^{1}H 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.[16] ^{1}H 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 ^{1}H and ^{13}C NMR spectroscopy. In addition, the color change of the catalyst with each

Scheme 1. 2-Methyl-2-oxazoline, Bis(1,3-dimethylimidazoline-2-ylidene)palladium(II) Diiodide, and Methyltriflate or 2,3-Dimethyl-2-oxazolinium Triflate Initiators for the Test Polymerization of 2-Methyl-2-oxazoline in the Presence of the NHC/Palladium Catalyst



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.[13] 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.[14] Therefore, compounds **1a**−**c** were treated with palladium(II) acetate in the presence of sodium iodide and KO^{t}Bu 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 ^{1}H 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-dimethylimidazoline-2-ylidene that was prepared according to a literature procedure[15] and were obtained as yellow solids. ^{13}C 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, ^{me}NCH***C***HN^{alk}, in addition to the signal at 122.9 ppm that can be assigned to the three other carbon atoms ^{me}N***C***HCHN^{alk} and ^{me}N***C***HCHN^{me}. ^{1}H NMR analysis shows two signals at 7.31 ppm which can be assigned to ^{me}NCHC***H***N^{alk} and a second signal at 7.28 ppm corresponding to ^{me}NC***H***CHN^{me} and ^{me}NC***H***CHN^{alk} 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 ^{1}H and ^{13}C NMR spectroscopy, MALDI-TOF, and elemental analysis. Figure 1 shows the ^{1}H NMR spectrum of **4c**. Characteristic are the two methylene groups of the oxazoline ring at 3.66 (−N−C***H***$_2$−) and 4.12 ppm

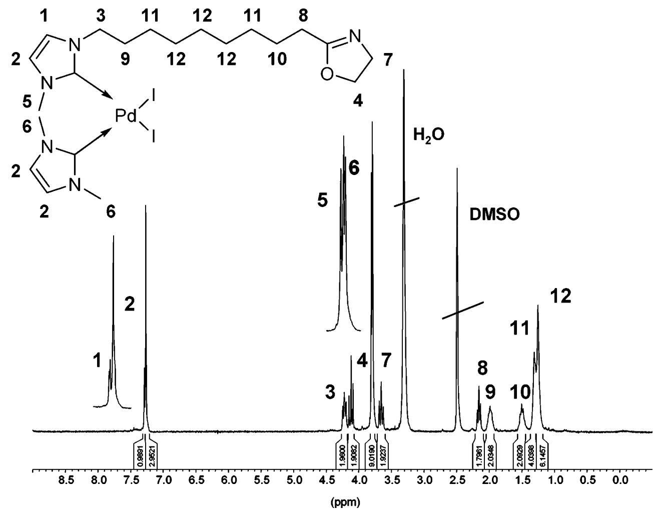
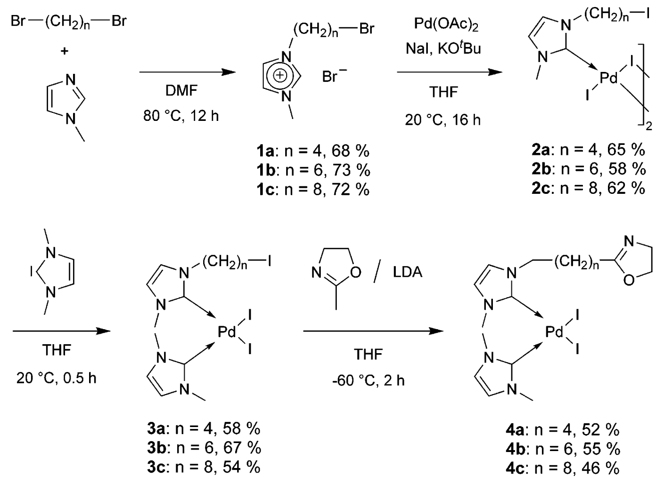


Figure 1. ^{1}H NMR spectrum of monomer **4c** (d_6-DMSO, 300.1 MHz, T = 20 °C).

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



(−O−C$\boldsymbol{H}_2$−). 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.[16] 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.

^{1}H NMR analysis indicated successful polymerization of the NHC/palladium catalyst carrying monomers. Quantitative analysis of polymer composition and palladium content as determined by ^{1}H 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 ^{1}H 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.[17a] 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.[17b]

4. Heck Reaction in Aqueous Media. Heck coupling of sp^2-halides with alkenes promoted by palladium catalysts is one of the most important methods for C−C coupling in organic synthesis,[18] the synthesis of important intermediates for pharmaceuticals,[19] and conducting polymers.[20] Although many efforts have been made to prepare heterogeneous Heck catalysts,[21] homogeneous catalysts still have many advantages on catalytic activity.[22] 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.[23]

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 $Pd(OAc)_2/PPh_3$ in pure aqueous solution and the beneficial effect of various tetrabutylammonium halides.[24] 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

Scheme 3. Synthesis of the NHC/Palladium-Functionalized Block Copolymers (TCE = tetrachloroethane)

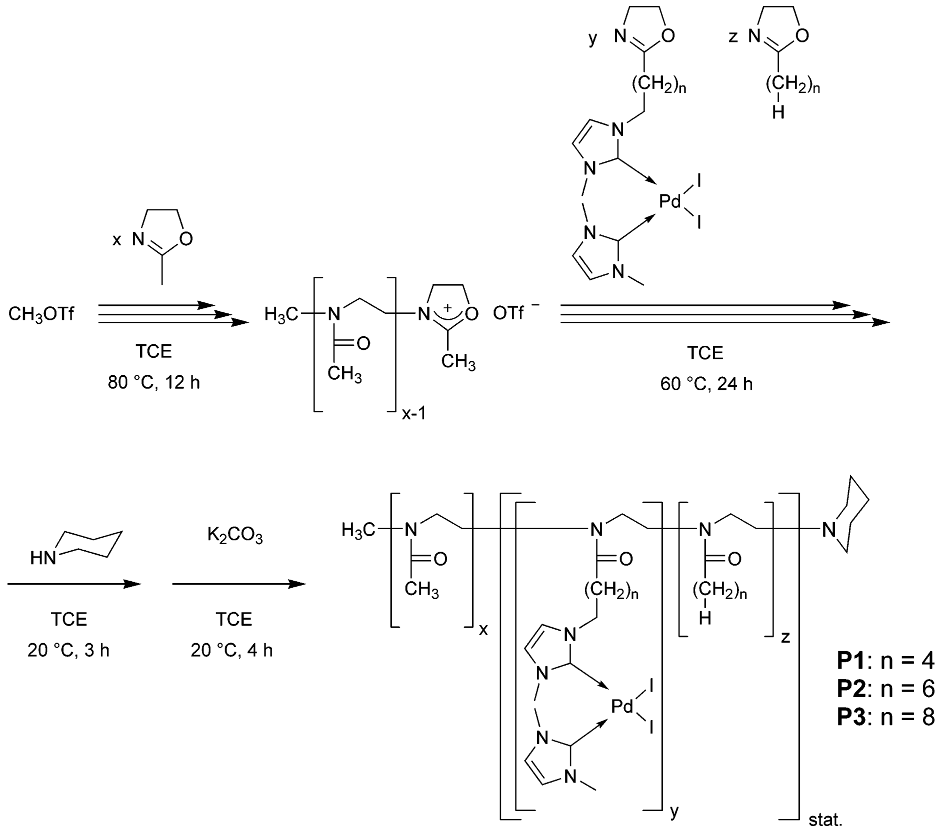


Table 1. Analytical Data of the Amphphilic Polymer Supports P1−P3

polymer	$x_{\text{exp,(calcd)}}$, NMR[a]	$y_{\text{exp,(calcd)}}$, NMR[a]	$z_{\text{exp,(calcd)}}$, NMR[a]	$\bar{M}_n$, NMR	PDI[b,c]	γ/%[d]
P1	28.4 (30.7)	1.5 (2.4)	2.9 (3.0)	3920 (2584)	1.32 (1.35)	3.3
P2	29.9 (32.2)	1.8 (2.7)	3.2 (3.2)	4400 (2661)	1.35 (1.33)	3.6
P3	30.4 (30.6)	1.9 (2.9)	3.4 (3.1)	4730 (2668)	1.39 (1.32)	3.6

[a] For meaning of *x*, *y*, and *z*, see Scheme 3. [b] As determined by GPC with poly(styrene) standards. [c] In brackets: $\bar{M}_n$ and PDI of the first block. [d] Palladium mass content as determined by ICP−OES.

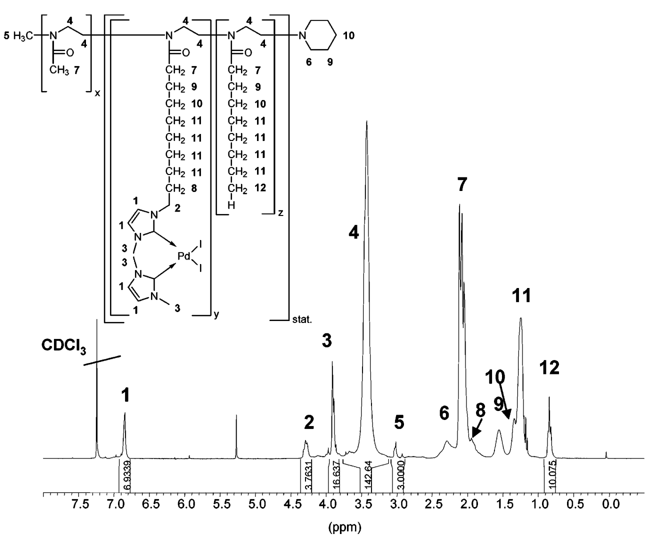


Figure 2. ^{1}H NMR of the soluble NHC/palladium-bound polymer **P3** ($CDCl_3$, 300.1 MHz, T = 20 °C).

with 10 mol % palladium catalyst showing excellent recyclability but poor activities (TOF < 1 h^{-1}).[7a]

Table 2. Hydrodynamic Radii of the Aggregates Formed by P1−P3 in Aqueous Solution

polymer	c_P (mM)	D_{app} (10^{-7} cm^2 s^{-1})	r_h (nm)
P1	0.24	1.50	14.2
P2	0.23	2.19	9.8
P3	0.20	0.69	30.7

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 K_2CO_3 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

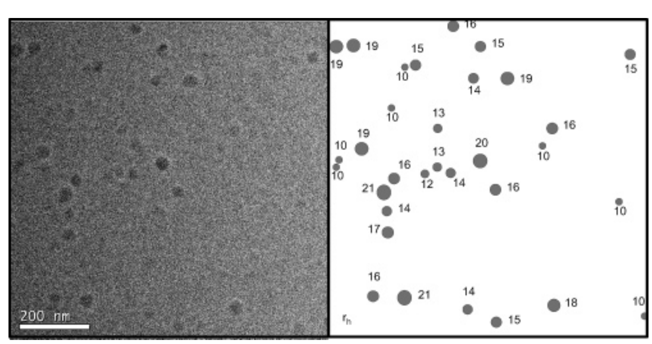


Figure 3. TEM micrograph of **P1** ($c_P = 2.5 \times 10^{-4}$ mol/L) with the hydrodynamic radii r_h of the aggregates observed.

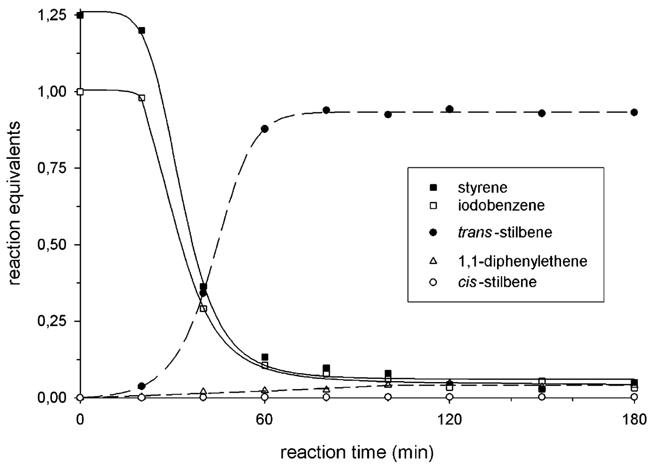


Figure 4. Kinetics of the Heck coupling of styrene and iodobenzene (PhI) at 90 °C (PhI:styrene:K_2CO_3 = 1.0:1.25:1.5, **P3** = 0.57 mM, n_{Pd}/n_{PhI} = 0.0067).

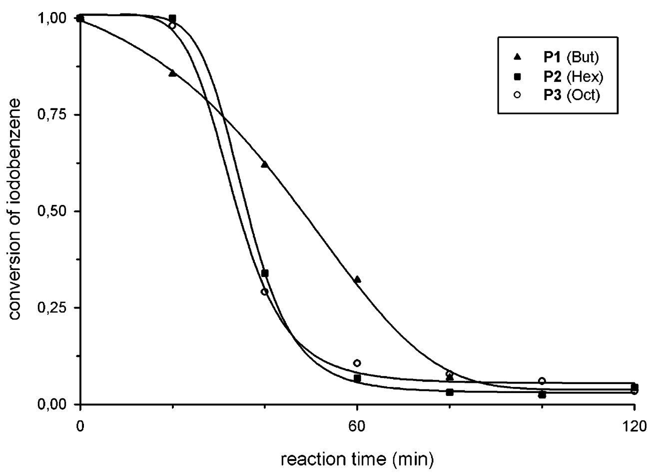


Figure 5. Reaction kinetics of the Heck coupling of iodobenzene (PhI) and styrene as a function of amphiphile **P1**–**P3** at T = 90 °C (PhI:styrene:K_2CO_3 = 1.0:1.25:1.5, c_P = 0.67 mM, n_{Pd}/n_{PhI} = 0.0067).

Table 3. Catalytic Results of the Heck Coupling of Iodobenzene (PhI) with Styrene with the Polymer-Bound Catalysts P1–P3 (PhI:styrene:K_2CO_3 = 1.0:1.25:1.5, c_P = 0.57 mM, n_{Pd}/n_{PhI} = 0.0067)

polymer	t (h)[a]	*trans*-stilbene (%)[b]	TOF (h^{-1})
P1	2	>93	150
P2	1.5	>93	570
P3	1.5	>93	530

[a] Reaction time. [b] *trans*-Stilbene as determined by gas chromatography.

TOF number as a measure of catalyst activity was determined to be 530 h^{-1} from the point of inflection (in comparison to the results of Uozumi et al. with a TOF value of 1 h^{-1} for the same substrates) and indicates the high activity of the soluble, polymer-bound NHC/palladium catalyst.

In the second set of experiments we studied **P1**–**P3** under the same conditions and thus the effect of spacer length on the catalytic performance. As can be visualized from Figure 5 and Table 3, catalytic transformation of iodobenzene in the presence of **P1** with the butyl spacer showed a very different kinetic behavior compared to **P2** and **P3**. Catalyst activity as determined by TOF values is in the case of **P1** by a factor of 3.5 lower compared to **P2** and **P3** (see Table 3). Most likely 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 °C.

Table 4. Catalytic Results of the Heck Coupling of Iodobenzene (PhI) with Styrene with the Polymer-Bound Catalysts P3 (PhI:styrene:K_2CO_3 = 1.0:1.25:1.5, c_P = 0.17 mM, n_{Pd}/n_{PhI} = 0.1 mol %, T = 90 °C)

cycle	t (h)[a]	conversion (%)	*trans*-stilbene (%)[b]
1	5	89	80
2	5	82	75
3	5	76	68

[a] Reaction time. [b] *trans*-Stilbene as determined by gas chromatography.

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.[4g] 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.[25]

In summary, we presented the first synthesis of amphiphilic, water-soluble block copolymers based on 2-oxazolines with pendent 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 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 ($\bar{P}_n$), 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_f).

Measurements. ^{1}H (300.13 MHz) and ^{13}C 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 Inorganic Institute of the 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-trihydroxyanthracene (dithranol) as matrix substance. UV−vis spectra were recorded on a Varian Cary 3 spectrometer. A Jobin 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, FID/1177. Melting points were measured using a Mettler FP51 melting point apparatus. The TEM micrographs were recorded at the Johannes-Gutenberg Universität in Mainz (Prof. M. Schmidt, Dr. K. Fischer) for this a FEI−Tecnai F30 ST apparatus was used. The dynamic light scattering (DLS) measurements were carried out at the Johannes-Gutenberg Universität in Mainz (Prof. M. Schmidt, Dr. K. Fischer) using a Uniphase He/Ne laser (λ = 632.8 nm, 22 mW), a ALV−SP 86 Goniometer, a ALV/High QE APD-Avalanche photodiode with fiber optic detection, a ALV300 correlator, and a Lauda RC-6 thermostatization unit.

Materials. All chemicals were purchased from Aldrich Chemical Co., Fluka, and Deutero and used as received, unless otherwise noted. Water-free solvents were purchased from Fluka (benzene, DMF) or dried by standard procedures (THF Na/benzophenone; diethyl ether, KOH molecular sieves 4 Å, BTS catalyst; HMPT CaH_2, P_2O_5; tetrachloroethane, metox, piperidine CaH_2) and stored under a dry nitrogen atmosphere and molecular sieves, 4 Å.

Synthesis of the Asymmetric Substituted Imidazolium Salts (1a−c). A portion of α,ω-dibromoalkane (200 mmol, 4 equiv) in 200 mL of DMF was placed in a 500 mL flask equipped with a 100 mL addition funnel. To the stirred mixture a solution of 4.11 g (50 mmol, 1 equiv) of *N*-methylimidazole in 20 mL of DMF was added dropwise within 4 h at 80 °C. Stirring was continued for a further 12 h at this temperature. The excess amount of α,ω-dibromoalkane can be recycled by fine vacuum distillation. The residue was purified by column chromatography (SiO_2, acetone:methanol = 3:1) to yield the desired imidazolium salt.

*1-(4-Bromobutyl)-3-methylimidazolium Bromide (**1a**)*. Yield 10.10 g (33.9 mmol, 68%), colorless viscous oil, r_f = 0.49. ^{1}H NMR (d_6-DMSO, 300.13 MHz, 20 °C): δ = 1.77 (tt, ^3J = 6.9 Hz, ^3J = 6.7 Hz, 2H; im-CH$_2$CH_2), 1.91 (tt, ^3J = 6.7 Hz, ^3J = 6.5 Hz, 2H; CH_2CH$_2$Br), 3.55 (t, ^3J = 6.5 Hz, 2H; CH_2Br), 3.85 (s, 3H; CH_3), 4.22 (t, ^3J = 6.9 Hz, 2H; im-CH_2), 7.73 (s, 1H; ^{me}NCH=CHN^{alk}), 7.80 (s, 1H; ^{me}NCH=CHN^{alk}), 9.21 (s, 1H; NCHN). ^{13}C NMR (d_6-DMSO, 75.47 MHz, 20 °C): δ = 28.4 (im-CH$_2$$CH_2$), 28.9 ($CH_2CH_2$Br), 34.3 ($CH_2$Br), 36.0 ($CH_3$), 48.0 (im-$CH_2$), 122.4 (^{me}NCH=$C$HN^{alk}), 123.8 (^{me}N$C$H=CHN^{alk}), 136.8 (N$C$HN). IR (ATR, substance): $\tilde{\nu}$ (cm^{-1}) = 3057 m (ν C$_{sp2}$−H), 2951 m (ν C$_{sp3}$−H), 2860 w (ν C$_{sp3}$−H), 1634 w (ν C⋯C, ν C⋯N), 1569 s (ν C⋯C, ν C⋯N), 1456 m (δ CH$_2$, δ_{as} CH$_3$), 1425 m (δ CH$_2$, δ_{as} CH$_3$), 1362 w (δ_s CH$_3$), 1259 m, 1237 w, 1165 vs (ν C−N), 1090 w, 1022 w, 872 m, 826 m, 764 s, 740 s, 644 s, 620 vs.

*1-(6-Bromohexyl)-3-methylimidazolium Bromide (**1b**)*. Yield 11.88 g (36.4 mmol, 73%), colorless viscous oil, r_f = 0.52. ^{1}H NMR (d_6-DMSO, 300.13 MHz, 20 °C): δ = 1.25 (tt, ^3J = 7.3 Hz, ^3J = 7.3 Hz, 2H; CH_2), 1.40 (tt, ^3J = 7.3 Hz, ^3J = 7.3 Hz, 2H; CH_2), 1.78 (tt, ^3J = 6.9 Hz, ^3J = 6.9 Hz, 4H; im-CH$_2$CH_2, CH_2CH$_2$Br), 3.52 (t, ^3J = 6.6 Hz, 2H; CH_2Br), 3.84 (s, 3H; CH_3), 4.15 (t, ^3J = 7.1 Hz, 2H; im-CH_2), 7.70 (s, 1H; ^{me}NCH=CHN^{alk}), 7.77 (s, 1H; ^{me}NCH=CHN^{alk}), 9.14 (s, 1H; NCHN). ^{13}C NMR (d_6-DMSO, 75.47 MHz, 20 °C): δ = 24.8 (CH$_2$), 27.0 (CH$_2$), 29.3 (im-CH$_2$$CH_2$), 32.1 ($CH_2$Br), 35.2 ($CH_2CH_2$Br), 35.9 ($CH_3$), 48.8 (im-$CH_2$), 122.4 (^{me}NCH=$C$HN^{alk}), 123.8 (^{me}N$C$H=CHN^{alk}), 136.7 (N$C$HN). IR (ATR, substance): $\tilde{\nu}$ (cm^{-1}) = 3056 m (ν C$_{sp2}$−H), 2940 s (ν C$_{sp3}$−H), 2857 m (ν C$_{sp3}$−H), 1634 w (ν C⋯C, ν C⋯N), 1570 s (ν C⋯C, ν C⋯N), 1459 m (δ CH$_2$, δ_{as} CH$_3$), 1430 m (δ CH$_2$, δ_{as} CH$_3$), 1378 w (δ_s CH$_3$) 1248 m, 1165 vs (ν C−N), 1092 w, 1020 w, 870 m, 824 m, 752 s, 725 m (γ CH$_2$, (CH$_2$)$_{n\geq4}$), 646 s, 620 vs.

*1-(8-Bromooctyl)-3-methylimidazolium Bromide (**1c**)*. Yield 12.68 g (35.8 mmol, 72%), colorless viscous oil, r_f = 0.54. ^{1}H NMR (d_6-DMSO, 300.13 MHz, 20 °C): δ = 1.26 (m, 6H; CH_2), 1.35 (m, 2H; CH_2), 1.77 (tt, ^3J = 6.9 Hz, ^3J = 6.9 Hz, 4H; im-CH$_2$CH_2, CH_2CH$_2$Br), 3.50 (t, ^3J = 6.7 Hz, 2H; CH_2Br), 3.85 (s, 3H; CH_3), 4.15 (t, ^3J = 7.1 Hz, 2H; im-CH_2), 7.71 (s, 1H; ^{me}NCH=CHN^{alk}), 7.78 (s, 1H; ^{me}NCH=CHN^{alk}), 9.19 (s, 1H; NCHN). ^{13}C NMR (d_6-DMSO, 75.47 MHz, 20 °C): δ = 25.5 (CH$_2$), 27.6 (CH$_2$), 28.0 (CH$_2$), 28.3 (CH$_2$), 29.5 (im-CH$_2$$CH_2$), 32.3 ($CH_2$Br), 35.4 ($CH_2CH_2$Br), 36.0 ($CH_3$), 48.9 (im-$CH_2$), 122.4 (^{me}NCH=$C$HN^{alk}), 123.8 (^{me}N$C$H=CHN^{alk}), 136.7 (N$C$HN). IR (ATR, substance): $\tilde{\nu}$ (cm^{-1}) = 3054 m (ν C$_{sp2}$−H), 2928 vs (ν C$_{sp3}$−H), 2854 s (ν C$_{sp3}$−H), 1630 w (ν C⋯C, ν C⋯N), 1568 s (ν C⋯C, ν C⋯N), 1460 s (δ CH$_2$, δ_{as} CH$_3$), 1432 m (δ CH$_2$, δ_{as} CH$_3$), 1378 w (δ_s CH$_3$), 1244 m, 1167 vs (ν C−N), 1091 w, 1024 w, 870 m, 828 m, 752 s, 725 s (γ CH$_2$, (CH$_2$)$_{n\geq4}$), 648 s, 621 vs.

Synthesis of the Dinuclear Palladium Complexes (2a−c). The imidazolium salt (**1a−c**, 22.3 mmol, 1 equiv), palladium acetate (5.00 g, 22.3 mmol, 1 equiv), KO^{t}Bu (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 filtered through silica using ethyl acetate as solvent to separate the polar byproducts. The resulting raw product was purified by column chromatography (SiO_2, ethyl acetate: hexane = 1:1).

*Di-μ-iodobis[1-(4′-iodobutyl)-3-methylimidazoline-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_f = 0.56. ^{1}H NMR (d_6-DMSO, 300.13 MHz, 20 °C): δ = 1.80 (tt, ^3J = 7.0 Hz, ^3J = 7.0 Hz, 4H; im-CH$_2$CH_2), 2.04 (tt, ^3J = 6.9 Hz, ^3J = 6.9 Hz, 4H; CH_2CH$_2$I), 3.28 (t, ^3J = 6.9 Hz, 4H; CH_2I), 3.73 (s, 6H; CH_3), 4.19 (t, ^3J = 7.0 Hz, 4H; im-CH_2), 7.42 (s, 4H; NCH=CHN). ^{13}C NMR (d_6-DMSO, 75.47 MHz, 20 °C): δ = 7.6 (CH$_2$I), 29.8 (CH$_2$CH$_2$I), 30.2 (im-CH$_2$$CH_2$), 38.6 ($CH_3$), 49.5 (im-$CH_2$), 123.0 (^{me}NCH=$C$HN^{alk}), 124.4 (^{me}N$C$H=CHN^{alk}), carbene signal not detected. IR (ATR, substance): $\tilde{\nu}$ (cm^{-1}) = 3122 m (ν C$_{sp2}$−H), 3031 vw (ν C$_{sp2}$−H), 2937 s (ν C$_{sp3}$−H), 2860 m (ν C$_{sp3}$−H), 1653 m (ν C⋯C, ν C⋯N), 1569 m (ν C⋯C, ν C⋯N), 1467 s (δ CH$_2$, δ_{as} CH$_3$), 1418 m (δ CH$_2$, δ_{as} CH$_3$), 1368 w (δ_s CH$_3$), 1261 m, 1228 s, 1204 m, 1170 m, 1117 m, 1084 m, 1014 w, 728 m (γ CH$_2$, (CH$_2$)$_{n\geq4}$), 669 vs.

*Di-μ-iodobis[1-(6′-iodohexyl)-3-methylimidazoline-2-ylidene]-dipalladium(II) Diiodide (**2b**)*. Yield 8.39 g (6.4 mmol, 58%), orange-colored solid, mp = 144.2 °C (± 1.0 °C), r_f = 0.64. ^{1}H NMR (d_6-DMSO, 300.13 MHz, 20 °C): δ = 1.36 (m, 8H; CH_2), 1.77 (tt, ^3J = 7.2 Hz, ^3J = 6.8 Hz, 4H; CH_2CH$_2$I), 1.99 (tt, ^3J = 7.3 Hz, ^3J = 6.9 Hz, 4H; im-CH$_2$CH_2), 3.26 (t, ^3J = 7.2 Hz, 4H; CH_2I), 3.73 (s, 6H; CH_3), 4.15 (t, ^3J = 7.3 Hz, 4H; im-CH_2), 7.41 (s, 2H; ^{me}NCH=CHN^{alk}), 7.42 (s, 2H; ^{me}NCH=CHN^{alk}). ^{13}C NMR (d_6-DMSO, 75.47 MHz, 20 °C): δ = 9.0 (CH$_2$I), 25.0 (CH$_2$), 28.6 (CH$_2$), 29.5 (CH$_2$), 32.9 (CH$_2$CH$_2$I), 38.5 (CH$_3$), 50.5 (im-CH$_2$), 123.0 (^{me}NCH=CHN^{alk}), 124.3 (^{me}NCH=CHN^{alk}), carbene signal not detected. IR (ATR, substance): $\tilde{\nu}$ (cm^{-1}) = 3124 w (ν C$_{sp2}$−H), 3033 vw (ν C$_{sp2}$−H), 2930 s (ν C$_{sp3}$−H), 2855 m (ν C$_{sp3}$−H), 1653 m (ν C⋯C), 1569 m (ν C⋯N), 1471 s (δ CH$_2$, δ_{as} CH$_3$), 1418 s (δ

CH_2, δ_{as} CH_3), 1368 w (δ_s CH_3), 1262 m, 1222 m, 1193 m, 1166 w, 1124 w, 1083 m, 1016 m, 803 m, 730 vs (γ CH_2, $(CH_2)_{n\geq 4}$), 670 vs.

*Di-μ-iodobis[1-(8′-iodooctyl)-3-methylimidazoline-2-ylidene]dipalladium(II) Diiodide (**2c**).* Yield 9.45 g (6.9 mmol, 62%), orange-colored solid, mp = 121.6 °C (± 1.0 °C), r_f = 0.69. ^{1}H NMR (d_6-DMSO, 300.13 MHz, 20 °C): δ = 1.31 (m, 16H; CH_2), 1.76 (tt, ^3J = 6.9 Hz, ^3J = 6.9 Hz, 4H; CH_2CH$_2$I), 1.92 (tt, ^3J = 7.3 Hz, ^3J = 7.0 Hz, 4H; im-CH$_2$CH_2), 3.25 (t, ^3J = 6.9 Hz, 4H; CH_2I), 3.72 (s, 6H; CH_3), 4.14 (t, ^3J = 7.3 Hz, 4H; im-CH_2), 7.40 (s, 2H; ^{me}NC*H*═CHN^{alk}), 7.41 (s, 2H; ^{me}NCH═C*H*N^{alk}). ^{13}C NMR (d_6-DMSO, 75.47 MHz, 20 °C): δ = 9.2 (CH$_2$I), 25.9 (CH$_2$), 27.8 (CH$_2$), 28.4 (CH$_2$), 28.7 (CH$_2$), 29.9 (CH$_2$), 33.0 (CH$_2$CH$_2$I), 38.5 (CH$_3$), 50.6 (im-CH$_2$), 122.9 (^{me}NCH═*C*HN^{alk}), 124.2 (^{me}N*C*H═CHN^{alk}), carbene signal not detected. IR (ATR, substance): $\tilde{\nu}$ (cm^{-1}) = 3124 w (ν C$_{sp2}$−H), 3032 vw (ν C$_{sp2}$−H), 2930 s (ν C$_{sp3}$−H), 2852 s (ν C$_{sp3}$−H), 1653 w (ν C$\cdots$C, ν C$\cdots$N), 1569 m (ν C$\cdots$C, ν C$\cdots$N), 1470 s (δ CH$_2$, δ_{as} CH$_3$), 1418 s (δ CH$_2$, δ_{as} CH$_3$), 1368 w (δ_s CH$_3$), 1263 s, 1221 s, 1204 m, 1182 m, 1117 w, 1082 m, 1015 m, 801 m, 731 vs (γ CH$_2$, $(CH_2)_{n\geq 4}$), 670 vs.

Synthesis of the Mononuclear Palladium Complexes (3a−c). 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-dimethylimidazoline-2-ylidene in 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 (SiO$_2$, ethyl acetate: hexane = 1:1).

*[1-(4′-Iodobutyl)-3-methylimidazoline-2-ylidene](1,3-dimethylimidazoline-2-ylidene)palladium(II) Diiodide (**3a**).* Yield 4.16 g (5.8 mmol, 58%), citrus-colored solid, mp = 208.0 °C (± 1.0 °C), r_f = 0.52. ^{1}H NMR (d_6-DMSO, 300.13 MHz, 20 °C): δ = 1.80 (tt, ^3J = 7.1 Hz, ^3J = 7.1 Hz, 2H; im-CH$_2$CH$_2$), 2.13 (tt, ^3J = 7.2 Hz, ^3J = 7.2 Hz, 4H; CH$_2$CH$_2$I), 3.27 (t, ^3J = 7.2 Hz, 2H; CH$_2$I), 3.79 (s, 6H; CH$_3$-car-CH$_3$), 3.82 (s, 3H; alk-car-CH$_3$), 4.27 (t, ^3J = 7.1 Hz, 2H; im-CH$_2$), 7.27 (s, 2H; ^{me}NCH═CHN^{me}), 7.29 (s, 1H; ^{me}NCH═CHN^{alk}), 7.31 (s, 1H; ^{me}NCH═CHN^{alk}). ^{13}C NMR (d_6-DMSO, 75.47 MHz, 20 °C): δ = 7.8 (CH$_2$I), 30.3 (CH$_2$), 30.5 (CH$_2$), 37.5 (CH$_3$), 37.6 (CH$_3$), 37.9 (CH$_3$), 49.0 (im-CH$_2$), 122.0 (^{me}NCH═CHN^{alk}), 122.9 (^{me}NCH═CHN^{me}, ^{me}NCH═CHN^{alk}), 166.6, 166.9 (^{me}NCN^{me}, ^{me}NCN^{alk}). IR (ATR, substance): $\tilde{\nu}$ (cm^{-1}) = 3115 w (ν C$_{sp2}$−H), 3032 vw (ν C$_{sp2}$−H), 2935 m (ν C$_{sp3}$−H), 2860 m (ν C$_{sp3}$−H), 1653 w (ν C$\cdots$C, ν C$\cdots$N), 1592 m (ν C$\cdots$C, ν C$\cdots$N), 1466 s (δ CH$_2$, δ_{as} CH$_3$), 1401 m (δ CH$_2$, δ_{as} CH$_3$), 1376 w (δ_s CH$_3$), 1264 s, 1223 s, 1175 m, 1110 m, 1077 m, 1011 w, 830 w, 734 s (γ CH$_2$, $(CH_2)_{n\geq 4}$), 696 vs.

*[1-(6′-Iodohexyl)-3-methylimidazolium-2-ylidene](1,3-dimethylimidazoline-2-ylidene)palladium(II) Diiodide (**3b**).* Yield 5.02 g (6.7 mmol, 67%), citrus-colored solid, mp = 193.8 °C (± 1.0 °C), r_f = 0.57. ^{1}H NMR (d_6-DMSO, 300.13 MHz, 20 °C): δ = 1.37 (m, 4H; CH$_2$), 1.76 (tt, ^3J = 7.2 Hz, ^3J = 6.7 Hz, 2H; CH$_2$CH$_2$I), 2.00 (tt, ^3J = 7.3 Hz, ^3J = 6.9 Hz, 2H; im-CH$_2$CH$_2$), 3.26 (t, ^3J = 6.9 Hz, 2H; CH$_2$I), 3.79 (s, 6H; CH$_3$-car-CH$_3$), 3.81 (s, 3H, alk-car-CH$_3$), 4.23 (t, ^3J = 7.3 Hz, 2H; im-CH$_2$), 7.28 (s, 3H; ^{me}NCH═CHN^{me}, ^{me}NCH═CHN^{alk}), 7.31 (s, 1H; ^{me}NCH═CHN^{alk}). ^{13}C NMR (d_6-DMSO, 75.47 MHz, 20 °C): δ = 9.1 (CH$_2$I), 25.2 (CH$_2$), 29.6 (CH$_2$), 29.6 (CH$_2$), 32.9 (CH$_2$CH$_2$I), 37.5 (CH$_3$), 37.6 (CH$_3$), 37.8 (CH$_3$), 50.2 (im-CH$_2$), 121.9 (^{me}NCH═CHN^{alk}), 122.9 (^{me}NCH═CHN^{me}, ^{me}NCH═CHN^{alk}), 166.6, 166.8 (^{me}NCN^{me}, ^{me}NCN^{alk}). IR (ATR, substance): $\tilde{\nu}$ (in cm^{-1}) = 3115 w (ν C$_{sp2}$−H), 3052 w (ν C$_{sp2}$−H), 2932 m (ν C$_{sp3}$−H), 2855 w (ν C$_{sp3}$−H), 1653 w (ν C$\cdots$C, ν C$\cdots$N), 1559 m (ν C$\cdots$C, ν C$\cdots$N), 1466 s (δ CH$_2$, δ_{as} CH$_3$), 1419 m (δ CH$_2$, δ_{as} CH$_3$), 1378 w (δ_s CH$_3$), 1264 s, 1225 m, 1170 w, 1112 w, 1078 m, 1012 w, 895 w, 733 vs (γ CH$_2$, $(CH_2)_{n\geq 4}$), 694 vs.

*[1-(8′-Iodooctyl)-3-methylimidazolium-2-ylidene](1,3-dimethylimidazoline-2-ylidene)palladium(II) Diiodide (**3c**).* Yield 4.21 g (5.4 mmol, 54%), citrus-colored solid, mp = 207.8 °C (± 1.0 °C), r_f = 0.64. ^{1}H NMR (d_6-DMSO, 300.13 MHz, 20 °C): δ = 1.31 (m, 8H; CH_2), 1.73 (tt, ^3J = 7.2 Hz, ^3J = 7.2 Hz, 2H; CH_2CH$_2$I), 1.99 (tt, ^3J = 7.4 Hz, ^3J = 6.9 Hz, 2H; im-CH$_2$CH_2), 3.25 (t, ^3J = 7.2 Hz, 2H; CH_2I), 3.79 (s, 6H; CH_3-car-CH_3), 3.81 (s, 3H; alk-car-CH_3), 4.22 (t, ^3J = 7.4 Hz, 2H; im-CH_2), 7.27 (s, 3H; ^{me}NC*H*═C*H*N^{me}, ^{me}NC*H*═CHN^{alk}), 7.29 (s, 1H; ^{me}NCH═C*H*N^{alk}). ^{13}C NMR (d_6-DMSO, 75.47 MHz, 20 °C): δ = 9.2 (CH$_2$I), 26.1 (CH$_2$), 27.9 (CH$_2$), 28.6 (CH$_2$), 29.7 (CH$_2$), 29.9 (CH$_2$), 33.0 (CH$_2$CH$_2$I), 37.4 (CH$_3$), 37.6 (CH$_3$), 37.8 (CH$_3$), 50.2 (im-CH$_2$), 121.9 (^{me}NCH═*C*HN^{alk}), 122.9 (^{me}N*C*H═*C*HN^{me}, $_{me}$N*C*H═CHN^{alk}), 166.6, 166.8 (^{me}N*C*N^{me}, ^{me}N*C*N^{alk}). IR (ATR, substance): $\tilde{\nu}$ (cm^{-1}) = 3124 vw (ν C$_{sp2}$−H), 3053 w (ν C$_{sp2}$−H), 2932 m (ν C$_{sp3}$−H), 2856 w (ν C$_{sp3}$−H), 1653 w (ν C$\cdots$C, ν C$\cdots$N), 1576 m (ν C$\cdots$C, ν C$\cdots$N), 1471 s (δ CH$_2$, δ_{as} CH$_3$), 1419 m (δ CH$_2$, δ_{as} CH$_3$), 1264 vs, 1225 s, 1078 m, 1014 w, 896 m, 731 vs (γ CH$_2$, $(CH_2)_{n\geq 4}$), 694 vs.

Synthesis of the Complex Functionalized 2-Oxazoline Monomers (4a−c). 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, which was cooled to −78 °C by a CO$_2$ (s)/acetone bath, was added dropwise 0.51 g (6.0 mmol, 1.5 equiv) of 2-methyl-2-oxazoline in 6 mL of THF within 20 min. The resulting reaction mixture was stirred for 2 h at −60 °C. Then 4.0 mmol (1 equiv) of the precursor (**3a**−**c**) 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. Afterward the solution was warmed to room temperature overnight, and the solvent was separated by rotary evaporation. The residue was purified by column chromatography (SiO$_2$, ethyl acetate:NEt$_3$ = 15:1) and freeze-dried using benzene.

*Monomer **4a**.* Yield 1.40 g (2.1 mmol, 52%), pale yellow-colored solid, r_f = 0.24. ^{1}H NMR (d_6-DMSO, 300.13 MHz, 20 °C): δ = 1.36 (tt, ^3J = 7.6 Hz, ^3J = 7.3 Hz, 2H; CH_2), 1.60 (tt, ^3J = 7.5 Hz, ^3J = 7.3 Hz, 2H; CH_2CH$_2$-ox), 2.01 (tt, ^3J = 7.5 Hz, ^3J = 7.3 Hz, 2H; im-CH$_2$CH_2), 2.20 (t, ^3J = 7.3 Hz, 2H; CH_2-ox), 3.67 (t, ^3J = 9.4 Hz, 2H; ═NCH_2), 3.78 (s, 6H; CH_3-car-CH_3), 3.81 (s, 3H; alk-car-CH_3), 4.14 (t, ^3J = 9.4 Hz, 2H; OCH_2), 4.22 (t, ^3J = 7.5 Hz, 2H; im-CH_2), 7.27 (s, 3H; ^{me}NC*H*═C*H*N^{me}, ^{me}NC*H*═CHN^{alk}), 7.29 (s, 1H; ^{me}NCH═C*H*N^{alk}). ^{13}C NMR (d_6-DMSO, 75.47 MHz, 20 °C): δ = 25.3 (CH$_2$), 25.8 (CH$_2$), 27.3 (im-CH$_2$$CH_2$), 29.5 ($CH_2$-ox), 37.4 ($CH_3$), 37.6 ($CH_3$), 37.8 ($CH_3$), 50.0 (im-$CH_2$), 54.0 (═N$CH_2$), 66.7 (O$CH_2$), 122.0 (^{me}NCH═*C*HN^{alk}), 122.9 (^{me}N*C*H═*C*HN^{me}, ^{me}N*C*H═CHN^{alk}), 166.3, 166.8, 166.9 (^{me}NCN^{me}, ^{me}N*C*N^{alk}, O*C*N). IR (ATR, substance): $\tilde{\nu}$ (cm^{-1}) = 3115 w (ν C$_{sp2}$−H), 3038 vw (ν C$_{sp2}$−H), 2933 m (ν C$_{sp3}$−H), 2868 w (ν C$_{sp3}$−H), 1663 s (ν C═N, ν C$\cdots$C, ν C$\cdots$N), 1568 m (ν C$\cdots$C, ν C$\cdots$N), 1466 s (δ CH$_2$, δ_{as} CH$_3$), 1400 m (δ CH$_2$, δ_{as} CH$_3$), 1265 m, 1223 s, 1077 m (ν_{as} C−O−C), 985 m (ν_s C−O−C), 958 m (ν_s C−O−C), 730 vs (γ CH$_2$, $(CH_2)_{n\geq 4}$), 695 s. MALDI-TOF (*m/z*): found 679.18, 550.59; calcd. 677.94 (M + H$^+$ = $C_{17}H_{28}I_2N_5OPd^+$), 550.03 (M − I$^-$ = $C_{17}H_{27}I_1N_5OPd^+$). Anal. Calcd: C, 30.13; H, 4.02; I, 37.45; N, 10.33; Pd, 15.70. Found: C, 30.57; H, 4.21; I, 36.98; N, 10.02; Pd, 15.88.

*Monomer **4b**.* Yield 1.54 g (2.2 mmol, 55%), pale yellow-colored solid, r_f = 0.31. ^{1}H NMR (d_6-DMSO, 300.13 MHz, 20 °C): δ = 1.31 (m, 6H; CH_2), 1.51 (tt, ^3J = 7.3 Hz, ^3J = 7.3 Hz, 2H; CH_2CH$_2$-ox), 1.99 (tt, ^3J = 7.4 Hz, ^3J = 7.4 Hz, 2H; im-CH$_2$CH_2), 2.16 (t, ^3J = 7.3 Hz, 2H; CH_2-ox), 3.66 (t, ^3J = 9.3 Hz, 2H; ═NCH_2), 3.78 (s, 6H; CH_3-car-CH_3), 3.81 (s, 3H; alk-car-CH_3), 4.12 (t, ^3J = 9.3 Hz, 2H; OCH_2), 4.22 (t, ^3J = 7.4 Hz, 2H; im-CH_2), 7.27 (s, 3H; ^{me}NC*H*═C*H*N^{me}, ^{me}NC*H*═CHN^{alk}), 7.29 (s, 1H; ^{me}NCH═C*H*N^{alk}). ^{13}C NMR (d_6-DMSO, 75.47 MHz, 20 °C): δ = 25.7 (CH$_2$), 26.1 (CH$_2$), 27.3 (CH$_2$CH$_2$-ox), 28.4 (CH$_2$), 28.6 (CH$_2$), 29.7 (CH$_2$-ox), 37.4 (CH$_3$), 37.6 (CH$_3$), 37.9 (CH$_3$), 50.2 (im-CH$_2$), 54.0 (═NCH$_2$), 66.7 (OCH$_2$), 121.9 (^{me}NCH═*C*HN^{alk}), 122.9 (^{me}N*C*H═*C*HN^{me}, ^{me}N*C*H═CHN^{alk}), 166.6, 166.8, 166.9 (^{me}NCN^{me}, ^{me}N*C*N^{alk}, O*C*N). IR (ATR, substance): $\tilde{\nu}$ (cm^{-1}) = 3054 w (ν C$_{sp2}$−H), 2977 w (ν C$_{sp3}$−H), 2943 m (ν C$_{sp3}$−H), 2869 m (ν C$_{sp3}$−H), 1660 s (ν C═N, ν C$\cdots$C, ν C$\cdots$N), 1558 m (ν C$\cdots$C, ν C$\cdots$N), 1489 s (δ CH$_2$, δ_{as} CH$_3$), 1457 m (δ CH$_2$, δ_{as} CH$_3$), 1264 vs, 1227 m, 1171 m, 1080 m (ν_{as} C−O−C), 990 m (ν_s C−O−C), 956 m (ν_s C−O−C), 896 m, 730 vs (γ CH$_2$, $(CH_2)_{n\geq 4}$), 695 vs. MALDI-TOF (*m/z*): found 707.78, 578.59; calcd 705.98 (M + H$^+$ = $C_{19}H_{32}I_2N_5OPd^+$), 578.06 (M − I$^-$ = $C_{19}H_{31}I_1N_5OPd^+$). Anal. Calcd: C, 32.34; H, 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 (1.9 mmol, 46%), pale yellow-colored solid, r_f = 0.40. ^{1}H NMR (d_6-DMSO, 300.13 MHz, 20 °C): δ = 1.25 (s_{br}, 6H; CH_2), 1.31 (s_{br}, 4H; CH_2), 1.50 (m, 2H; CH_2CH$_2$-ox), 1.99 (m, 2H; im-CH$_2$CH_2), 2.16 (t, ^3J = 7.4 Hz, 2H; CH_2-ox), 3.66 (t, ^3J = 9.4 Hz, 2H; =NCH_2), 3.78 (s, 6H; CH_3-car-CH_3), 3.81 (s, 3H; alk-car-CH_3), 4.12 (t, ^3J = 9.4 Hz, 2H; OCH_2), 4.22 (t, ^3J = 7.5 Hz, 2H; im-CH_2), 7.26 (s, 3H; ^{me}NCH=CHN^{me}, ^{me}NCH=CHN^{alk}), 7.28 (s, 1H; ^{me}NCH=CHN^{alk}). ^{13}C NMR (d_6-DMSO, 75.47 MHz, 20 °C): δ = 25.6 (CH$_2$), 26.3 (CH$_2$), 27.3 (CH$_2$), 28.7 (CH$_2$), 28.8 (CH$_2$), 28.8 (CH$_2$), 29.0 (CH$_2$), 29.8 (CH$_2$), 37.4 (CH$_3$), 37.6 (CH$_3$), 37.8 (CH$_3$), 50.2 (im-CH$_2$), 54.0 (=NCH$_2$), 66.7 (OCH$_2$), 121.9 (^{me}NCH=CHN^{alk}), 122.9 (^{me}NCH=CHN^{me}, ^{me}NCH=CHN^{alk}), 166.7, 166.8, 166.9 (^{me}NCN^{me}, ^{me}NCN^{alk}, OCN). IR (ATR, substance): $\tilde{\nu}$ (cm^{-1}) = 3053 w (ν C$_{sp2}$−H), 2985 w (ν C$_{sp3}$−H), 2932 m (ν C$_{sp3}$−H), 2855 w (ν C$_{sp3}$−H), 1670 s (ν C=N, ν C$\cdots$C, ν C$\cdots$N), 1559 s (ν C$\cdots$C, ν C$\cdots$N), 1489 s (δ CH$_2$, δ_{as} CH$_3$), 1457 m (δ CH$_2$, δ_{as} CH$_3$), 1264 vs, 1227 m, 1163 m, 1078 m (ν_{as} C−O−C), 990 m (ν_s C−O−C), 956 w (ν_s C−O−C), 896 m, 731 vs (γ CH$_2$, (CH$_2$)$_{n\geq4}$), 702 vs MALDI-TOF (m/z): found 735.92, 606.65; calcd 734.01 (M + H$^+$ = $C_{21}H_{36}I_2N_5OPd^+$), 606.09 (M − I$^-$ = $C_{21}H_{35}I_1N_5OPd^+$). Anal. Calcd: C, 34.37; H, 4.81; I, 34.59; N, 9.54; Pd, 14.50. Found: C, 34.82; H, 4.94; I, 34.04; N, 9.82; Pd, 14.38.

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 30 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**, 2.5 equiv) as well as the corresponding unfunctionalized 2-alkyl-2-oxazoline (2.5 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 30 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 insoluble in diethyl ether.

P1. Yield 0.59 g (83%), citrus-colored solid. $\bar{P}_n$ (determined by ^{1}H NMR end-group analysis): (metox)$_{28.4}$[(**4a**)$_{1.5}$(butox)$_{2.9}$]$_{stat.}$ ($\bar{M}_n$ = 3920 g·mol^{-1}). SEC (CHCl$_3$, RI, poly(styrene) calibration): hydrophilic block $\bar{M}_n$= 1380 g·mol^{-1}, $\bar{M}_w$= 1870 g·mol^{-1}, PDI = 1.35; block copolymer $\bar{M}_n$ = 2410 g·mol^{-1}, $\bar{M}_w$ = 3190 g·mol^{-1}, PDI = 1.32. ICP−OES (Pd): 3.3%$_m$, $\bar{P}_n$(**4a**) = 1.2. ^{1}H NMR (CDCl$_3$, 300.13 MHz, 20 °C): δ = 0.88 (t_{br}; butox-CH_3), 1.31 (s_{br}; CH_2), 1.40 (s_{br}; CH_2), 1.54 (s_{br}; COCH$_2$CH_2), 1.67 (s_{br}; pip-C^3H_2), 1.90 (s_{br}; car-CH$_2$CH_2), 2.05, 2.08, 2.11 (s, s, s; COCH_3, COCH_2), 2.32 (s_{br}; pip-C^2H_2), 2.92 (s; CH_3-end group, Z$_{CH3,\ C=O}$), 3.02 (s; CH_3-end group, E$_{CH3,C=O}$), 3.43 (s_{br}; CH_2-backbone), 3.91 (s_{br}; car-CH_3), 4.30 (t_{br}; car-CH_2), 6.86 (s_{br}; NCH=CHN). ^{13}C NMR (CDCl$_3$, 75.47 MHz, 20 °C), signal groups: δ = 13.9 (butox-CH$_3$), 21.1−21.7 (COCH$_3$), 22.5 (CH$_2$), 27.2−27.5 (CH$_2$), 29.6 (CH$_2$), 32.2 (COCH$_2$), 38.1−38.4 (car-CH$_3$), 43.4−44.2 (CH$_2$-backbone), 44.9−45.6 (CH$_2$-backbone), 46.5−47.2 (CH$_2$-backbone), 47.3−48.3 (CH$_2$-backbone), 52.4 (car-CH$_2$), 122.2−122.4 (NCH=CHN), 170.4−171.4 (C=O). UV−vis (H$_2$O, c = 0.2 g·L^{-1}, d = 1 cm): block copolymer λ (ϵ in cm^2 mmol^{-1}) = 200−243 (>20 000; polymer), 262 (13 000; car), 300 (15 800; PdI$_2$), shoulder: 330 (6000) to 410 (520), 440−900 (<300); hydrophilic block λ (ϵ) = 200−226 (>20 000; polymer), 262 (1300), 300 (700), 380−900 (<300).

P2. Yield 0.56 g (84%), citrus-colored solid. $\bar{P}_n$ (determined by ^{1}H NMR end-group analysis): (metox)$_{29.9}$[(**4b**)$_{1.8}$(hexox)$_{3.2}$]$_{stat.}$ ($\bar{M}_n$ = 4400 g·mol^{-1}). SEC (CHCl$_3$, RI, poly(styrene) calibration): hydrophilic block $\bar{M}_n$ = 1260 g·mol^{-1}, $\bar{M}_w$ = 1680 g·mol^{-1}, PDI = 1.33; block copolymer $\bar{M}_n$ = 2790 g·mol^{-1}, $\bar{M}_w$= 3770 g·mol^{-1}, PDI = 1.35. ICP−OES (Pd): 3.6%$_m$, $\bar{P}_n$(**4b**) = 1.5. ^{1}H NMR (CDCl$_3$, 300.13 MHz, 20 °C): δ = 0.85 (t, ^3J = 6.1 Hz; hexox-CH_3), 1.26 (s_{br}; CH_2), 1.36 (s_{br}; CH_2), 1.56 (s_{br}; COCH$_2$CH_2, pip-C^3H_2), 1.97 (s_{br}; car-CH$_2$CH_2), 2.05, 2.08, 2.11 (s, s, s; COCH_3, COCH_2), 2.32 (s_{br}; pip-C^2H_2), 2.92 (s; CH_3-end group, Z$_{CH3,C=O}$), 3.02 (s; CH_3-end group, E$_{CH3,C=O}$), 3.43 (s_{br}; CH_2-backbone), 3.91 (s_{br}; car-CH_3), 4.29 (t, ^3J = 7.0 Hz; car-CH_2), 6.85 (s_{br}; NCH=CHN). ^{13}C NMR (CDCl$_3$, 75.47 MHz, 20 °C), signal groups: δ = 14.1 (hexox-CH$_3$), 21.1 (metox-COCH$_3$), 22.5 (CH$_2$), 24.9−25.6 (CH$_2$), 28.7−29.3 (CH$_2$), 31.5−31.7 (COCH$_2$, CH$_2$), 38.2−38.4 (car-CH$_3$), 43.4−44.2 (CH$_2$-backbone), 44.9−45.5 (CH$_2$-backbone), 46.5−47.2 (CH$_2$-backbone), 47.4−48.1 (CH$_2$-backbone), 51.1 (car-CH$_2$), 122.2−122.4 (NCH=CHN), 170.6−171.7 (C=O). UV−vis (H$_2$O, c = 0.2 g·L^{-1}, d = 1 cm): block copolymer λ (ϵ in cm^2·mmol^{-1}) = 200−244 (>20 000; polymer), 262 (15 900; car), 302 (18 600; PdI$_2$), 330$_S$ (7300) to 410$_S$ (600), 460−900 (<300); hydrophilic block λ (ϵ) = 200−226 (>20 000; polymer), 262 (1300), 300 (700), 380−900 (<300).

P3. Yield 0.63 g (88%), citrus-colored solid. $\bar{P}_n$ (determined by ^{1}H NMR end-group analysis): (metox)$_{30.4}$[(**4c**)$_{1.9}$(octox)$_{3.4}$]$_{stat.}$ ($\bar{M}_n$ = 4730 g·mol^{-1}). SEC (CHCl$_3$, RI, poly(styrene) calibration): hydrophilic block $\bar{M}_n$ = 1330 g·mol^{-1}, $\bar{M}_w$ = 1760 g·mol^{-1}, PDI = 1.32; block copolymer $\bar{M}_n$= 2970 g·mol^{-1}, $\bar{M}_w$= 4140 g·mol^{-1}, PDI = 1.39. ICP−OES (Pd): 3.6%$_m$, $\bar{P}_n$(**4c**) = 1.6. ^{1}H NMR (CDCl$_3$, 300.13 MHz, 20 °C): δ = 0.84 (t, ^3J = 6.1 Hz; octox-CH_3), 1.25 (s_{br}; CH_2), 1.34 (s_{br}; CH_2), 1.56 (s_{br}; COCH$_2$CH_2, pip-C^3H_2), 2.00 (s_{br}; car-CH$_2$CH_2), 2.05, 2.08, 2.11 (s, s, s; COCH_3, COCH_2), 2.30 (s_{br}; pip-C^2H_2), 2.92 (s; CH_3-end group, Z$_{CH3,C=O}$), 3.02 (s; CH_3-end group, E$_{CH3,C=O}$), 3.43 (s_{br}; CH_2-backbone), 3.90 (s_{br}; car-CH_3), 4.29 (t, ^3J = 7.1 Hz; car-CH_2), 6.85 (s_{br}; NCH=CHN). ^{13}C NMR (CDCl$_3$, 75.47 MHz, 20 °C), signal groups: δ = 14.1 (octox-CH$_3$), 21.0−21.3 (metox-COCH$_3$), 22.6 (CH$_2$), 25.2−25.5 (CH$_2$), 26.8 (CH$_2$), 29.1−29.5 (CH$_2$), 31.8 (COCH$_2$, CH$_2$), 38.2 − 38.5 (car-CH$_3$), 43.4−43.9 (CH$_2$-backbone), 44.8−45.7 (CH$_2$-backbone), 46.3−47.2 (CH$_2$-backbone), 47.5−48.1 (CH$_2$-backbone), 51.1−51.3 (car-CH$_2$), 122.2−122.5 (NCH=CHN), 170.6−171.5 (C=O). UV−vis (H$_2$O, c = 0.2 g·L^{-1}, d = 1 cm): block copolymer λ (ϵ in cm^2·mmol^{-1}) = 200−247 (>20 000; polymer), 262 (17 400; car), 302 (16 300; PdI$_2$), 330$_S$ (7100) to 410$_S$ (700), 570−900 (<300); hydrophilic block λ (ϵ) = 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 (50, 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 = 340.458 nm, atom line). The background was measured at λ = 340.4163 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 0.1−0.6 mm. Iodobenzene, potassium carbonate as base, and tetradecane as internal standard were added (iodobenzene:styrene:K$_2$CO$_3$ = 1:1.25:1.5). 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.

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