Functionalization of Amphiphilic Poly(2-oxazoline) Block Copolymers: A Novel Class of Macroligands for Micellar Catalysis[†]

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ABSTRACT: A new class of amphiphilic poly(2-oxazoline) block copolymers bearing triphenylphosphine moieties has been synthesized. In aqueous media, these polymers form functionalized micelles with transition metal binding sites located in the hydrophobic core, thereby forming a catalytic active microreactor. The triphenylphosphine moieties were selectively introduced into the hydrophobic block by polymer analogous Pd-catalyzed phosphorus−carbon coupling reaction. The corresponding polymer precursor was prepared by living cationic polymerization of 2-methyl-2-oxazoline forming the hydrophilic part and statistical copolymerization of 2-heptyl-2-oxazoline and *ω*-iodoarylheptyl-2-oxazoline for the functionalized hydrophobic segment. This route allows a direct control of the number of the ligand functions by the ratio of the two hydrophobic monomers.

Introduction

Amphiphilic block copolymers have attracted much interest due to their behavior at the air/water interface and their aggregation in water into micellar structures.[1] The use of powerful synthetic tools such as living polymerization systems enables the preparation of a broad variety of different block copolymer architectures.[2] Such amphiphilic block copolymers represent an interesting extension to the common low molar mass surfactants because the choice of the different monomers and the ratio of the block length allow a good control of the hydrophilic/lipophilic balance (HLB). Moreover, synthetic polymers offer the possibility to selectively introduce additional functions along the polymer chain. This can be done either at both terminal ends or within the chain.

We are especially interested in the polymerization of 2-oxazolines due to the good control of the molar mass with low polydispersities[3] at the desired range of functionalization. Block copolymers can easily be synthesized by the so-called "one-pot-multistage" technique.[4] Recently, we demonstrated examples for selective end-group functionalization using the initiator[5] as well as the termination method.[6]

The functionalization, we are especially interested in, is a ligand moiety for transition metals[7] useful for catalytic reactions.[12]

By the selective introduction of such binding sites into the hydrophobic segment of an amphiphilic block copolymer, polydental macromolecular ligands should be formed, which aggregate in water and form micelles. These micelles do not only solubilize water-insoluble organic molecules but also act as microreactor due to the catalyst in the hydrophobic micellar core (compare with Figure 1). This concept of micellar catalysis[8] combines the advantages of the homogeneous and the heterogeneous processes. After the reaction the aqueous phase polymer bound catalyst[9] can be separated from the organic phase products, even if the amphiphilic polymer might impair the phase separation.

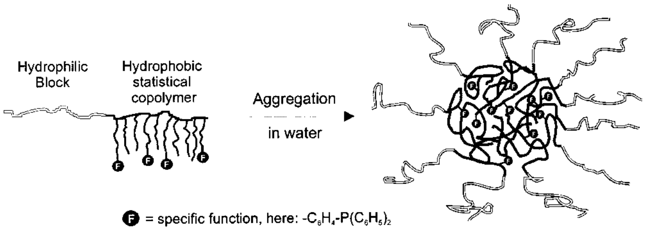

Figure 1. Tentative picture of the aggregation of functionalized amphiphilic polymers in water.

Catalysis in biphasic systems[10] (mixture of aqueous catalyst phase and organic product phase) was successfully realized in the hydroformylation reaction of propene, known as the *Ruhrchemie/Rhone-Poulenc process.[11]* The main problem of the synthesis of higher aldehydes via this route is the poor water solubility of higher olefins. This problem can be avoided by micellar catalysis because the catalyst is fixed in a hydrophobic environment by the amphiphilic polymer.

For this purpose triphenylphosphine derivatives are suitable ligands since they are widely used in homogeneous catalysis.[12] The scope of this contribution is the introduction of the triphenylphosphine moiety into the hydrophobic block of a poly(2-oxazoline) block copolymer (general structure according to Scheme 1) using functionalized monomers without impairing the living polymerization reaction. The living cationic polymerization mechanism of the 2-oxazoline system allows the variation of many structural parameters: r, p, q, R_1, and R_2 as depicted in Scheme 1 and Table 1. Because of this, it is possible to adjust the different properties i.e., water solubility, cmc, ligand density.

Experimental Part

Instrumentation. ^{1}H NMR (300 MHz), ^{31}P NMR (75 MHz), and ^{13}C NMR (60 MHz) spectra were obtained on a Bruker ARX 300 spectrometer. FT-IR spectroscopy was carried out on a Bruker IFS 55 spectrometer. Elemental analysis were measured by the Microanalytical Laboratory of the "Anorganisch-chemisches Institut" of the TU München. The fluorescence analysis for the determination of the critical micelle concentration (cmc) was performed on a Spex FLUORlog

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[†] Dedicated Rolf C. Schulz on the occasion of his 80th birthday.

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Scheme 1. Synthesis of the Functionalized Block Copolymer

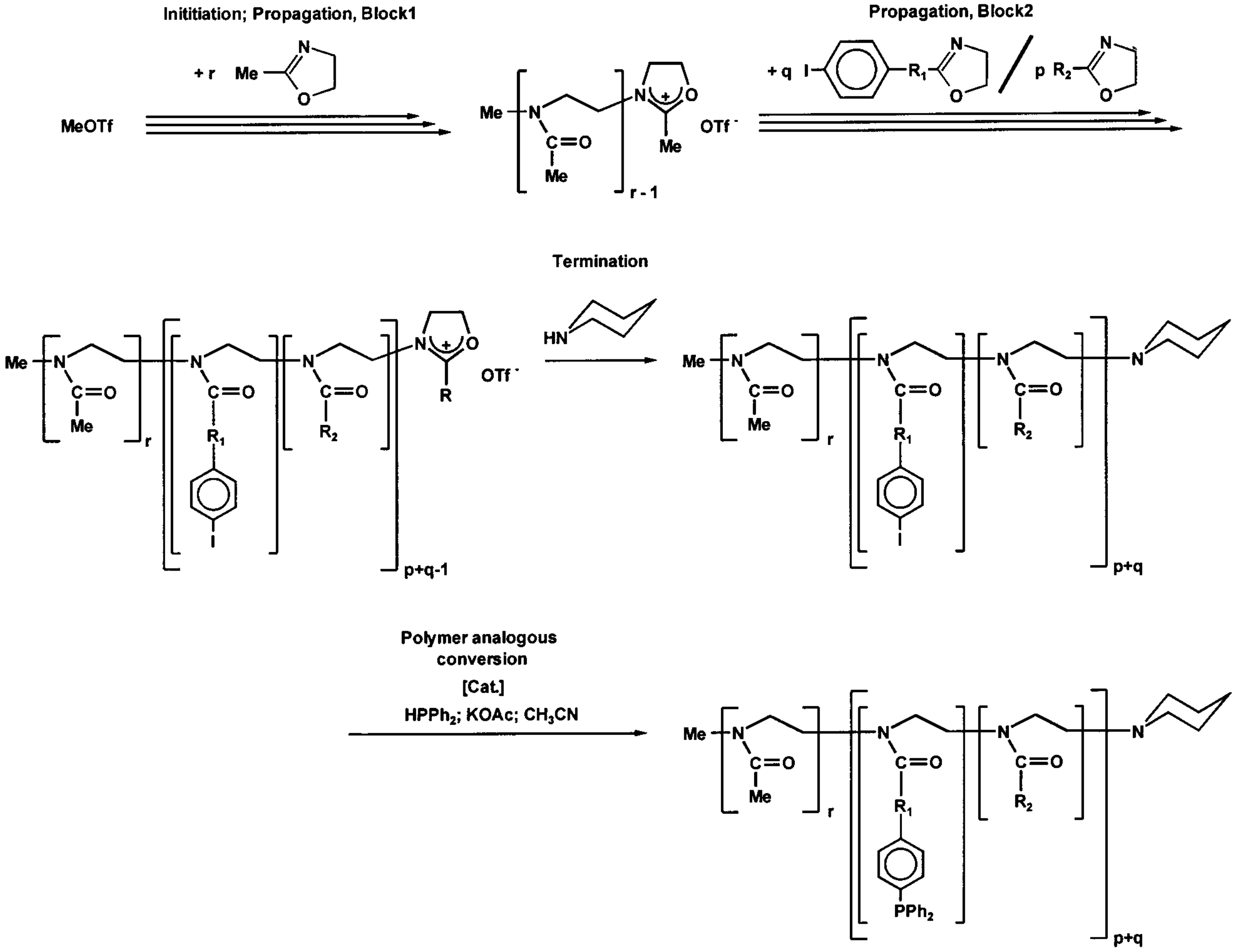


Table 1. Analytical Data for the Polymer Precursor

polymer	r_{cal}	p_{cal}	q_{cal}	$r_{exp,NMR}$	$p_{exp,NMR}$	$q_{exp,NMR}$	$M_{n,\ NMR}$	$M_{n,\ GPC}$	PDI[a]	cmc[b]
MeOx$_{30}$**3**$_6$	28.9	0	6.0	28.7	0	5.8	4790	4050	1.10	0.36
MeOx$_{30}$(**3**$_4$**1**$_2$)	30.0	2.0	4.0	30.2	2.0	3.9	4520	4240	1.13	0.70
MeOx$_{30}$(**3**$_2$**1**$_4$)	29.5	4.1	2.0	26.4	3.6	1.8	3650	2990	1.14	0.78

[a] By GPC. [b] In μmol/L ± 0.2 μmol/L.

spectrometer. Polymer solutions were prepared in a concentration range from 10^{-3} to 10^{-10} mol/L with carefully dried polymer and 0.2 μM solution of the fluorescence dye 6-*p*-toluidine-2-naphthylsulfonic acid in bidistilled water. Gel permeation chromatography (GPC) was carried out on a Waters GPC 510 equipped with an UV and RI-detector and using polystyrene standards for calibration and chloroform as eluent.

Monomers. *2-Heptyl-2-oxazoline (**1**)* was synthesized according to Seeliger et al.[13]

1-(4-Iodophenoxy)-6-bromohexane **(2).** To a solution of 11 g (50 mmol) of 4-iodophenol in 250 mL of acetone were added 15 g of finely grounded potassium carbonate and 48.8 g (0.2 mol, 4 equiv) of 1,6-dibromohexane. The mixture was refluxed overnight. At room temperature the mixture was poured into 200 mL of water and extracted three times with 200 mL of diethyl ether. The combined organic phases were washed with 1 N NaOH$_{aq}$ and water and dried with magnesium sulfate. The solvent and the excess of dibromohexane were removed by vacuum distillation.

Yield: 17.43 g (91%), colorless liquid, bp = 130 °C at 8.4 × 10^{-3} mbar.

IR (film): υ (cm^{-1}) = 3082, 3010, 2920, 2848, 1575, 1570, 1486, 1471, 1284, 1243, 1175, 822.

^{1}H NMR (CDCl$_3$): δ (ppm) = 7.52 (d, 2H, $^{3}J_{H,H}$ = 8.78 Hz, C$H_{ar.}$CI); 6.65 (d, 2H, $^{3}J_{H,H}$ = 8.77 Hz, C$H_{ar.}$COR); 3.89 (t, 2H, $^{3}J_{H,H}$ = 6.49 Hz, −CH$_2$CH_2O−); 3.37 (d, 2H, $^{3}J_{H,H}$ = 6.51 Hz, BrCH_2CH$_2$); 1.84 (tt, 2H, $^{3}J_{H,H}$ = 6.50 Hz, −CH$_2$CH_2CH$_2$O−); 1.74 (tt, 2H, $^{3}J_{H,H}$ = 6.51 Hz, CH$_2$CH_2CH$_2$Br); 1.45−1.30 (m, 4H, −CH_2CH$_2$CH$_2$Br, −CH_2CH$_2$CH$_2$O−).

^{13}C NMR (CDCl$_3$): δ (ppm) = 159.3 (C$_{ar}$−OR); 138.6 (C_{ar}−CI); 117.3 (C_{ar}−COR); 82.9 (C$_{ar}$−I); 68.2 (−C$_6$H$_4$OCH$_2$−); 34.2 (BrCH$_2$$CH_2$−); 33.0 (Br$CH_2$−); 29.4 (−OCH$_2$$CH_2$−); 28.3 (BrCH$_2$-CH$_2$$CH_2$−); 25.7 (−OCH$_2CH_2$$CH_2$−).

*2-(7-(4-Iodo)phenoxyheptyl)-2-oxazoline (IPP7) (**3**).* In a carefully dried flask under inert atmosphere 3.73 g (43.8 mmol) of 2-methyl-2-oxazoline and 100 mL of THF were cooled to −78 °C (CO$_{2(s)}$/acetone). 26.3 mL of a 2 N lithium diisopropylamide (LDA) solution was added dropwise over a period of 0.5 h and stirred for 2 h. After additional stirring (1 h, −20 °C), a solution of 16.78 g of 1-(4-iodophenoxy)-6-bromohexane (**2**) in 50 mL of dry THF was added dropwise. The resulting deeply red solution was allowed to warm to room temperature and stirred overnight. The reaction mixture was poured into 300 mL of ice−water and extracted three times with 200 mL of diethyl ether. The combined organic layers were washed with ice−water and dried with magnesium sulfate. The solvent was removed, and the residue was purified by flash chromatography (silica gel 60 (70−230 mesh, Fluka), ethyl acetate/hexane/triethylamine = 10:5:1). The colorless solid was freeze-dried from benzene.

Yield: 7.65 g (45%), colorless solid, mp = 60.4 °C.

IR (KBr): υ (cm^{-1}) = 3084, 3028, 2933, 2850, 1669, 1585, 1570, 1487, 1465, 1284, 1242, 984, 953, 818.

^{1}H NMR (CDCl$_3$): δ (ppm) = 7.51 (d, 2H, $^3J_{\mathrm{H,H}} = 8.78$ Hz, C$H_{\mathrm{ar.}}$CI); 6.64 (d, 2H, $^3J_{\mathrm{H,H}} = 8.75$ Hz, C$H_{\mathrm{ar.}}$COR); 4.20 (t, 2H, $^3J_{\mathrm{H,H}} = 9.55$ Hz, RC=NCH$_2$CH_2O−); 3.88 (t, 2H, $^3J_{\mathrm{H,H}} = 6.49$ Hz, −CH$_2$CH_2O−); 3.80 (t, 2H, $^3J_{\mathrm{H,H}} = 9.60$ Hz, RC=NCH_2CH$_2$O−); 2.25 (t, 2H, $^3J_{\mathrm{H,H}} = 7.63$ Hz, −CH_2C(OCH$_2$−)=NCH$_2$−); 1.74 (m, 2H, −CH_2CH$_2$O−); 1.61 (m, 2H, −CH_2CH$_2$C(OCH$_2$−)=NCH$_2$−); 1.45−1.30 (m, 6H, −OCH$_2$CH$_2$(CH_2)$_3$CH$_2$−).

^{13}C NMR (CDCl$_3$): δ (ppm) = 168.5 (RCON); 158.9 (C$_{\mathrm{ar}}$−OR); 138.1 (C_{ar}−CI); 116.9 (C_{ar}−COR); 82.4 (C$_{\mathrm{ar}}$−I); 68.0 (−C$_6$H$_4$OCH$_2$−); 67.1 (RC=NCH$_2$$CH_2$O−); 54.3 (RC=N$CH_2CH_2$O−); 29.0, 29.0, 28.9 (−$CH_2CH_2$O; −$CH_2$(CH$_2$)$_3$O; −$CH_2$C(OCH$_2$−)=NCH$_2$−); 27.9 ($CH_2CH_2$C(OCH$_2$−)=NCH$_2$−); 25.8 (−OCH$_2CH_2$$CH_2$−); 25.7($CH_2CH_2CH_2$C(OCH$_2$−)=NCH$_2$−).

$C_{16}H_{22}INO_2$ (387.24): Calcd (%): C, 49.63; H, 5.73; I, 32.77; N, 3.62. Found (%): C, 49.52; H, 5.57; I, 32.08; N, 3.30.

Polymerization. All polymerizations were carried out in a Schlenk tube under inert atmosphere (N$_2$) using freshly distilled and dried solvents.

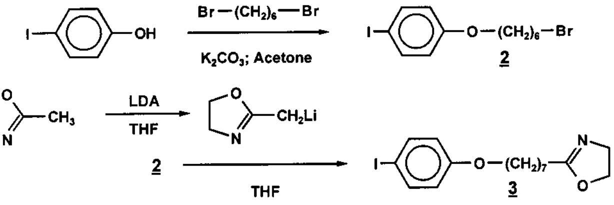
The general procedure was as follows: To a solution of 202 mg (1.23 mmol) of methyltriflate in 40 mL of acetonitrile was added 3.10 g (36.40 mmol, for $r = 30$) of 2-methyl-2-oxazoline (MeOx) at room temperature. The reaction mixture was stirred at 80 °C for 24 h. At room temperature, 0.416 g (2.46 mmol, $p = 2$) of 2-heptyl-2-oxazoline (**1**) and 1.905 g (4.92 mmol, $q = 4$) of **3** were added. The clear solution was stirred at 95 °C for an additional 24 h. At room temperature 310 mg (3.64 mmol, 3 equiv) of piperidine as terminating agent was added, and the mixture was stirred for 3 h. After removal of the solvent the residue was dissolved in 10 mL of chloroform, 2 g of potassium carbonate was added, and the mixture was stirred overnight. After filtration, the polymer was purified by reprecipitation (diethyl ether).

P−C Coupling Reaction. The general procedure was as follows: 2.5 g of polymer MeOx$_{30}$**1**$_2$**3**$_4$ (2.25 mmol of iodoaryl compound), 530 mg (5.4 mmol, 2.4 equiv) of potassium acetate, and 8.44 mg of Pd catalyst were combined in a Schlenk tube under an inert atmosphere. A 10 mL aliquot of acetonitrile was added, and the mixture was degassed. After addition of 838 mg (4.5 mmol, 2 equiv) of diphenylphosphine, the reaction mixture was heated to 110 °C. The ongoing reaction was monitored by ^{1}H NMR spectroscopy on crude fractions of the reaction mixture collected at room temperature. Complete conversion was typically observed after 48 h. After removal of the solvent the residue was dissolved in 10 mL of chloroform, 2 g of potassium carbonate was added, and the mixture was stirred overnight. After filtration (0.45 μm pore diameter, PTFA, Sartorius), the polymer was purified by reprecipitation (diethyl ether) under inert atmosphere.

Results and Discussion

The use of functionalized monomers enables the selective introduction of a desired moiety into the polymer. However, to maintain the described advantages of the living polymerization, it is necessary that no interaction between the propagation species and the function moiety of the monomer occurs. In the case of triphenylphosphine, the nucleophilic phosphorus might attack the positively charged active species (oxazolinium triflate) and thus impair the living polymerization. In model reactions, we found that in the presence of triphenylphosphine the concentration of the active species slowly decreases, especially at the end of the polymerization due to the lower monomer concentration.[14] Until now, this side reaction restricted the use of triphenylphosphine functionalized 2-oxazolines as monomers for cationic living polymerization reactions, although they are well-known as hard/soft bidental ligands in catalysis.[15] This problem can be solved by the introduction of the triphenylphosphine moiety after the polymerization step by a polymer analogous reaction.

Scheme 2. Synthesis of the Functionalized Monomer



In 1996, Stelzer et al. reported on a new reaction to synthesize triphenylphosphines by the palladium-catalyzed P−C coupling reaction.[16] The advantage of this reaction is that only small catalytic amounts of palladium are needed, and the reaction between an iodoaryl compound and the diarylphosphine is complete after a few hours.

This reaction can be directly applied for the preparation of the desired macromolecular ligands, synthesizing a 2-oxazoline monomer equipped with the appropriate iodoaryl moiety which do not react with the propagating oxazolinium species. Therefore, the synthesis of the desired polymers was carried out via this route as outlined in Scheme 1.

The synthesis of the 2-oxazoline monomer with the iodoaryl moiety is shown in Scheme 2.

Starting from 4-iodophenol, 1-(4-iodophenoxy)-6-bromohexane (**2**) was obtained by classical ether synthesis with 1,6-dibromohexane using an excess of the halide in order to avoid 1,6-bis(4-iodophenoxy)hexane. The unreacted 1,6-dibromohexane was simply removed by distillation. The final product 2-(7-(4-iodo)phenoxyheptyl)-2-oxazoline (**3**) (**IPP7** = iodo-*p*-phenyl-**7**) was obtained by the reaction of the lithiated 2-methyl-2-oxazoline with **2**. Successful isolation by means of column chromatography was possible using ethyl acetate/hexanes/triethylamine as the liquid phase and silica treated with the basic solvent mixture before use. This deactivation of silica is necessary since **3** is rather sensitive toward acids. 2-(7-(4-Iodo)phenoxyheptyl)-2-oxazoline (**3**) was isolated with a yield of 42% over both steps.

To demonstrate the feasibility of our concept, the possible variation parameters r, R_1, R_2, and ($p + q = 6$) were fixed, and only the ratio (p:q) of the two hydrophobic monomers was varied. Since the electronic and sterical properties of both monomers are very similar, it is reasonable to assume a solely statistical copolymerization of the two monomers similar to results reported by Litt et al.[17] A minimum length of a hydrophilic block ($r = 30$) is needed to obtain a sufficient water dispersibility of the entire polymer amphiphile.[18]

Piperidine was found to be a highly effective termination agent.[19] A quantitative neutralization of the quaternized nitrogen at the end group is necessary in order to maintain a comparable micellization behavior.

The results of the polymer syntheses are summarized in Table 1. All polymers exhibit a low polydispersity index (PDI) with high total yields (>90%) due to the optimized reaction conditions. In all cases, the desired ratios of the different monomers were obtained as determined by ^{1}H NMR spectroscopy.

However, all values of M_n and M_w as determined by gel permeation chromatography (GPC) tend to be too low due to the calibration using polystyrene standards. The amphiphilic character is demonstrated by the good

Table 2. Analytical Data for the Synthesized Macroligands

polymer	functionalization (%)	δ^a (^{31}P NMR)	r_{exp}	p_{exp}	q_{exp}	$M_{\mathrm{n,\,NMR}}$	PDI^b	cmc^c
MeOx$_{30}$**PP7**$_6$	>98	−5.76	28.7	0	5.8	5130	1.10	*d*
MeOx$_{30}$(**PP7**$_4$**1**$_2$)	>98	−5.74	30.2	2.0	3.9	4750	1.13	0.74
MeOx$_{30}$(**PP7**$_2$**1**$_4$)	>98	−5.73	26.4	3.6	1.8	3760	1.14	*d*

[a] In ppm. [b] By GPC. [c] In μmol/L ± 0.2 μmol/L. [d] Not measured.

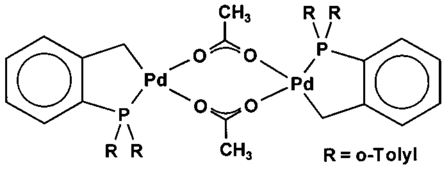


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Figure 2. Palladacyclus **4** by Herrmann et al.[21]

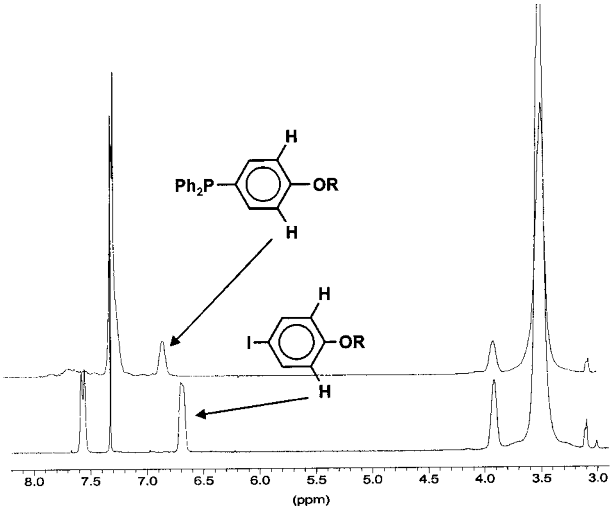

Figure 3. Conversion of the polymer precursor, monitored by ^{1}H NMR spectroscopy.

dispersibility in water (more than 1 mmol/L) and the low critical micelle concentration values (cmc), typical for nonionic polymer surfactants.

To estimate the yield of the polymer analogous functionalization reaction, the synthesis of the triphenylphosphine moiety was first tested with 4-iodophenol as a model compound. The conversion could easily be monitored by means of ^{1}H NMR spectroscopy. The doublet for the protons in the ortho position to the OR group at 6.65 ppm vanishes, and the new doublet appears at 6.85 ppm (compare with Figure 3). Additionally, a characteristic signal in the ^{31}P NMR at −5.4 ppm was observed. In accordance with earlier findings,[20] we demonstrated that the palladium compound **4**[21] as catalyst (Figure 2) leads to a faster and more selective formation of the phosphine in comparison with Pd(OAc)$_2$ used by Stelzer et al.[16]

In a first run with the polymeric iodoaryl compound we used 2.5 equiv of diphenylphosphine and a catalyst **4** to iodoaryl compound ratio of 1:100. The reaction was complete after 14 h at 110 °C. It is noteworthy that no decomposition of the polymer structure could be detected by means of NMR-spectroscopy. With significantly smaller amounts of catalyst (1:500) and of diphenylphosphine (1.25 equiv), the reaction was complete after 48 h (Figure 3). Obviously, the amount of side products was lower (mixture was less colored than in the first run). After purification of the polymers, in ^{31}P NMR spectra only the signal originating from the polymer bound phosphine could be seen, indicating that the amount of palladium left in the material is low. Furthermore, no side reactions accountable to the presence of palladium could be observed in successive catalysis experiments.[22] A quantification of the amount of palladium in the material by mass spectrometry is currently under investigation. The results of the macroligand syntheses are summarized in Table 2.

Conclusion

A new class of polymer ligands based on poly(2-oxazolines) with triphenylphosphine moieties has been successfully prepared by palladium-catalyzed phosphorus−carbon coupling. This is the first application of this reaction with polymeric iodoaromatic compounds yielding poly(2-oxazoline) block copolymers with triphenylphosphine moieties. This polymer system allows the variation of many parameters and thus the tuning of the desired properties. The average number of triphenylphosphine groups among a polymer chain can easily be varied by the ratio of the two hydrophobic monomers. The synthesized polymers exhibit properties typical of nonionic polymer amphiphiles, high water solubility, and low cmc values. We are currently investigating the impact of the variation of the polymer composition upon the performance of the polymer ligands, especially in the catalytic hydroformylation of higher olefins. Many other catalysis experiments such as Pd-catalyzed C−C coupling reactions are, in principle, accessible with these amphiphilic ligands. Furthermore, the living polymerization route allows structural variations, such as the introduction of the triphenylphosphine moiety at the end of a polymer chain (telechele) or functionalized gradient block copolymers.

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