

Preparation of Palladium Colloids in Block Copolymer Micelles and Their Use for the Catalysis of the Heck Reaction

S. Klingelhöfer,[†] W. Heitz,[†] A. Greiner,[†] S. Oestreich,[‡] S. Förster,[‡] and M. Antonietti^{*‡}

Contribution from the Fachbereich Physikalische Chemie der Universität Marburg/Polymere, Hans Meerwein Strasse, D-35032 Marburg, Germany, and Max Planck Institute of Colloids and Interfaces, Kantstrasse 55, D-14513 Teltow-Seehof, Germany

Received May 6, 1997[⊗]

Abstract: Colloidal dispersions of nanometer sized palladium colloids with very high stability were prepared in block copolymer micelles of polystyrene-*b*-poly-4-vinylpyridine and analyzed by electron microscopy and X-ray analysis. The resulting polymer/metal hybrids can easily be dissolved and handled in standard organic solvents such as toluene, tetrahydrofuran, and cyclohexane. They were successfully used for the Pd-catalyzed carbon–carbon coupling of aryl halides with alkenes (Heck reaction). Such block copolymer stabilized palladium colloids exhibit about the same reactivity as low molecular weight Pd complexes classically used for the Heck reaction, but show a much higher stability: in most reactions, the hybrids remain catalytically active even after 50000 turn-over cycles. Reaction rates were significantly controlled by the reactivity of the educts, but also respond to micelle architecture and dispersity of the palladium. Other advantages of the block copolymer stabilizer are that they are more simple and readily accessible than the phosphor-containing chelates, and that they dissolve even in “simple” solvents such as toluene (instead of amidic solvents).

Introduction

In the last years, the interest in the synthesis and properties of colloidal metal particles and metal clusters has grown constantly because of their unique properties. For noble metal colloids, especially catalytic applications are considered, since a unique combination of reactivity, stability, and selectivity is expected.^{1–3} The colloidal character of the dispersed noble metals adds some features to a catalyst which are not achieved by other metal dispersions: such systems have large specific areas (up to 3000 m²/cm³), their electronic states and transitions can be adjusted by the colloid size, and they can be doped and fine-tuned by appropriate, surface-bound ligands or mixed-in secondary components and metals.

Some of the current approaches to use metal clusters and colloids as catalysts for chemical and photochemical reactions were recently reviewed.^{4,5} It was also shown that colloid formation is the essential step in platinum-catalyzed hydrosilylation.⁶ Various noble metal colloids stabilized by surfactants and solvents were used for hydrogenation reactions.^{7–9} Even enantioselective hydrogenation reactions on noble metal colloids with chiral ligands have been performed.¹⁰ In a recent publication, Hermann and co-workers used palladium colloids as

effective catalysts for the Heck reaction, but also reported on some deficiencies in the long time stability related to the insufficient colloidal stabilization of the applied systems.¹¹ Similar observations were made by Reetz and co-workers.¹² The controlled generation of Pd colloids is also promising for a number of other reactions, such as oxidative conversions and cyclizations.^{13–15}

The deficiencies of the colloidal catalysts used up to now point to the rather general problem that formation of metal colloids is still far from being sufficiently well handled. Two main problems can be identified: On the one hand, it is still a desired goal to improve the control of particle size, particle size distribution, and structure of the metal colloids, since these quantities affect the catalytic properties. On the other hand, stabilization of the colloids is also far from being ideal, and quantities like durability in catalytic reactions are directly related to a more efficient particle stabilization.

The advantages and disadvantages of a variety of different methods for the preparation and stabilization of metal colloids were discussed in detail in a previous publication.¹⁶ There, it was also demonstrated that a very promising strategy toward stable and active noble metal nanoparticles is the preparation within the micelles of amphiphilic block copolymers, such as formed by polystyrene-*b*-poly-4-vinylpyridine (PS-*b*-P4VP) in selective solvents.^{17,18} Here, the micelle cores can be considered as a nanosized reaction vessel (the nanoreactor concept) for

[†] Fachbereich Physikalische Chemie der Universität Marburg/Polymer.

[‡] Max Planck Institute of Colloids and Interfaces.

[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1997.

- (1) Henglein, A. *Chem. Rev.* **1989**, *89*, 186.
- (2) Oggawa, S.; Hayashi, Y.; Kobayashi, N.; Tokizaki, T.; Nakamura, A. *Jpn. J. Appl. Phys.* **1994**, *33*, L331.
- (3) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693.
- (4) Belloni, J. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 184.
- (5) Bönnemann, H.; Braun, G.; Brijoux, W.; Brinkmann, R.; Schulze Tilling, A.; Seevogel, K.; Siepen, K. *J. Organomet. Chem.* **1996**, *520*, 143.
- (6) Lewis, L. N.; Lewis, L. *J. Am. Chem. Soc.* **1986**, *108*, 7228.
- (7) Henglein, A.; Ershov, B. G.; Malow, M. *J. Phys. Chem.* **1995**, *99*, 14129.
- (8) Toshima, N.; Yonezawa, T.; Kushihashi, K. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2537.
- (9) Schmid, G.; West, H.; Malm, J. O.; Bovin, J. O.; Grenthe, C. *Chem. Eur. J.* **1996**, *2*, 1099.
- (10) Bönnemann, H.; Braun, G. *Angew. Chem.* **1996**, *108*, 2120.

- (11) Beller, M.; Fischer, H.; Kuhlein, K.; Reisinger, C. P.; Herrmann, W. A. *J. Organomet. Chem.* **1996**, *520*, 257.
- (12) Reetz, M. T.; Lohmer, G. *Chem. Commun.* **1996**, *16*, 1921–1922.
- (13) VanBenthem, R. A. T. M.; Hiemstra, H.; VanLeeuwen, P. W. N. M.; Geus, J. W.; Speckamp, W. N. *Angew. Chem., Int. Ed. Engl.* **1995**, *34* (4), 457–460.
- (14) Larock, R. C.; Hightower, T. R.; Hasvold, L. A.; Peterson, K. P. *J. Org. Chem.* **1996**, *61*, 3584–3585.
- (15) Rönn, M.; Andersson, P. G.; Bäckvall, J. E. *Tetrahedron Lett.* **1997**, *38* (20), 3603–3606.
- (16) Antonietti, M.; Wenz, E.; Bronstein, L.; Seregina, M. *Adv. Mater.* **1995**, *7*, 1000.
- (17) Antonietti, M.; Heinz, S.; Rosenauer, C.; Schmidt, M. *Macromolecules* **1994**, *27*, 3276.

Table 1. Colloid-Analytical Data of the Polystyrene-*b*-poly-4-vinylpyridine Block Copolymers Used^a

polymer	M_n/g mol ⁻¹	M_w/g mol ⁻¹	$D = M_w/M_n$	f_{4VP}	$d_h/nm; \sigma$
PS-3.3	17500	20150	1.15	0.27	27.2; 0.121
PS-5.2	28014	36736	1.311	0.54	64.0; 0.112
PS-7.1	21200	21760	1.027	0.49	57.3; 0.096
PS-11.1	18980	19850	1.05	0.28	34.6; 0.278

^a M_n and M_w are number and weight averaged molecular weights, respectively; D denotes the polydispersity index. These quantities were determined by DMF-GPC. f_{4VP} is the relative amount of 4-VP ("core") in each micelle. The hydrodynamic diameter of the micelles in toluene, d_h , and the Gaussian width of its distribution, σ , as determined by dynamic light scattering are given in the last column.

metal colloids formation. The resulting hybrids between block copolymer micelles and metal colloids can be regarded as molecular entities which inherited the profitable solution behavior of polymers and the catalytic activity of metal colloids.

In some publications,^{16,19,20} it was shown for various noble metals that the colloid size depends on the micelle size and the molar ratio of metal to 4-vinylpyridine, but is mainly controlled by the type of reducing agent applied. In all cases, the stability of the formed colloids turned out to be very high, which is directly related to the stabilization of the final metal particles by a shell of block copolymer. Application of Pd, Pt, and Au monometallic and bimetallic nanoparticles as catalysts in the hydrogenation reaction of cyclohexene, 1,3-cyclooctadiene, and 1,3-cyclohexadiene was also examined.¹⁹ Selected colloidal catalysts showed about the same reactivity as commercial, optimized systems, but possessed a much higher stability and selectivity.

In the present paper, we want to focus on a more demanding synthesis, namely the Heck reaction of aryl halides with alkenes, which represents an important synthetic method in organic as well as in polymer chemistry.^{21,22} In most cases the Heck reaction is restricted to bromo- or iodoarenes. The usage of chloroarenes is still a challenging demand due to economic considerations, but is realized just for some systems with an otherwise high reactivity.^{23,24} In polymer chemistry the Heck reaction is also used for the synthesis of conjugated polymers for electronic and optical applications, where traces of residual palladium may ruin the electrooptical properties. For this application, small catalyst amounts relative to the educts and a good removability after reaction are advantageous. For both purposes, employment of block copolymer stabilized colloidal catalysts seems to be promising.

Experimental Section

The anionic synthesis of PS-*b*-P4VP block copolymers was carried out by the procedure described elsewhere.^{17,18} For the preparation of metal colloids, four different PS-*b*-P4VP block copolymers were chosen. Their molecular characteristics are summarized in Table 1.

Na_2PdCl_4 , superhydride ($\text{LiB}(\text{C}_2\text{H}_5)_3\text{H}$), haloarenes, olefins, tetradecane, and the different solvents were obtained from Aldrich and used as received (except tetradecane, which was distilled prior to use). Pd-

(18) Förster, S.; Zisenis, M.; Wenz, E.; Antonietti, M. *J. Chem. Phys.* **1996**, *104*, 9956.

(19) Serigina, M.; Bronstein, L.; Platonova, O. A.; Chernyshov, D. M.; Valetsky, P. M.; Wenz, E.; Hartmann, J.; Antonietti, M. *Chem. Mater.* **1997**, *9* (4), 923–931.

(20) Spatz, J. P.; Mössmer, S.; Möller, M. *Chem. Eur. J.* **1996**, *2*, 1552.

(21) Heck, R. F. *Org. React.* **1982**, *27*, 345.

(22) Greiner, A.; Heitz, W. *The Polymeric Materials Encyclopedia*; Salomone, J. C., Ed.; CRC Press: Boca Raton, 1996; Vol. 7, p 4865.

(23) Ben-David, Y.; Portnoy, M.; Gozin, M.; Milstein, D. *Organometallics* **1992**, *11*, 1995.

(24) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1655, 1665.

(OAc)₂ was obtained from Degussa and used as received. Tri-*o*-tolylphosphine (TOP) was prepared following a procedure described elsewhere.²⁵

Preparation of Colloidal Palladium Catalysts. A 250-mL three-necked flask equipped with a gas inlet, a bubbler, and a septum was evacuated several times and then filled with argon. In an argon stream, 0.5 g of the desired block copolymer and 100 mL of toluene (previously stored over sodium wire) were charged into the flask. After complete dissolution of the polymer, palladium acetate (0.25 mol of Pd(OAc)₂ per mol of 4-VP) was added to the solution. After being stirred over night (solubilization), the solution was degassed and superhydride (2 mol of superhydride per mol of Pd(OAc)₂ as 1 M LiB(C₂H₅)₃H in THF) was added through a septum to the yellow solution. The resulting dark brown solution was stored under argon.

Heck-Coupling Reactions. Heck-coupling reactions of haloarenes (generally 20 mmol) and olefins in toluene (typically 45 mL) with tri-*n*-butylamine (NBu₃) as base and different Pd catalyst systems and tetradecane as internal standard were carried out in lab-autoclaves under inert gas conditions. Other reaction parameters were varied as listed in Tables 2 and 3. Workup was accomplished by pouring samples of the reaction mixture into 2 N HCl, followed by extraction with toluene, drying over Na₂SO₄, and GC analysis.

Results and Discussion

Preparation of Metal Colloids. Solutions of palladium colloids—prepared as shown above—are stable for months and can be precipitated and redissolved without changing the colloidal properties. This is already a significant advantage compared to low molecular weight catalysts which require rapid consumption within days after their synthesis.

It was shown in preceding publications that the number and size of the metal particles in the micelle core is strongly affected by the reducing agent used. Reduction of the solubilized Pd(OAc)₂ by superhydride ($\text{LiB}(\text{C}_2\text{H}_5)_3\text{H}$) leads to a fast nucleation and growth of metal colloids in the micelle cores resulting in a so-called raspberry morphology. Here, a large number of small noble metal colloids or clusters (ca. 10–1000) are formed in each micelle core.^{16,19} This morphology offers a very high colloid surface area, is X-ray amorphous due to the small crystallites, and turned out to be the most appropriate morphology for hydrogenation and disproportionation reactions. For a better illustration and understanding of the following discussion, Figure 1 depicts electron micrographs of three arrays of dried block copolymer micelles with Pd colloids reduced by different reducing agents.

All three different degrees of dispersity were used as catalysts in the Heck reaction, and it turned out that the reduction with "fresh" superhydride leads to the most active catalyst systems, related to the finest distribution of Pd inside the micelle core. In this publication we will mainly discuss the Pd colloids reduced by "fresh" superhydride.

Pd-Catalyzed Coupling Reactions of Haloarenes and Olefins.

To evaluate the catalytic activity of block copolymer stabilized Pd colloids, Heck reactions were performed under different reaction conditions. In some cases, we also tested the reproducibility of the procedure of catalyst production, which turned out to be satisfactory (e.g. see Table 2, entry 6 and Table 3 entries 7, 10, and 11). Reexamination of the produced colloids by dynamic light scattering and TEM showed the same particle size and dispersion, i.e. the procedure is general and allows for direct repetition. This is important in the whole area of colloidal catalysts. In a first set of experiments with the system (PS-3.3, Pd) as a reference block copolymer catalyst, significantly different reactivities were found for different educts, as listed in Table 2. High reaction temperatures were necessary with

(25) Sander, R.; Klingelhöfer, S.; Hopmeier, M.; Göbel, E. O.; Heitz, W.; Greiner, A. In preparation.

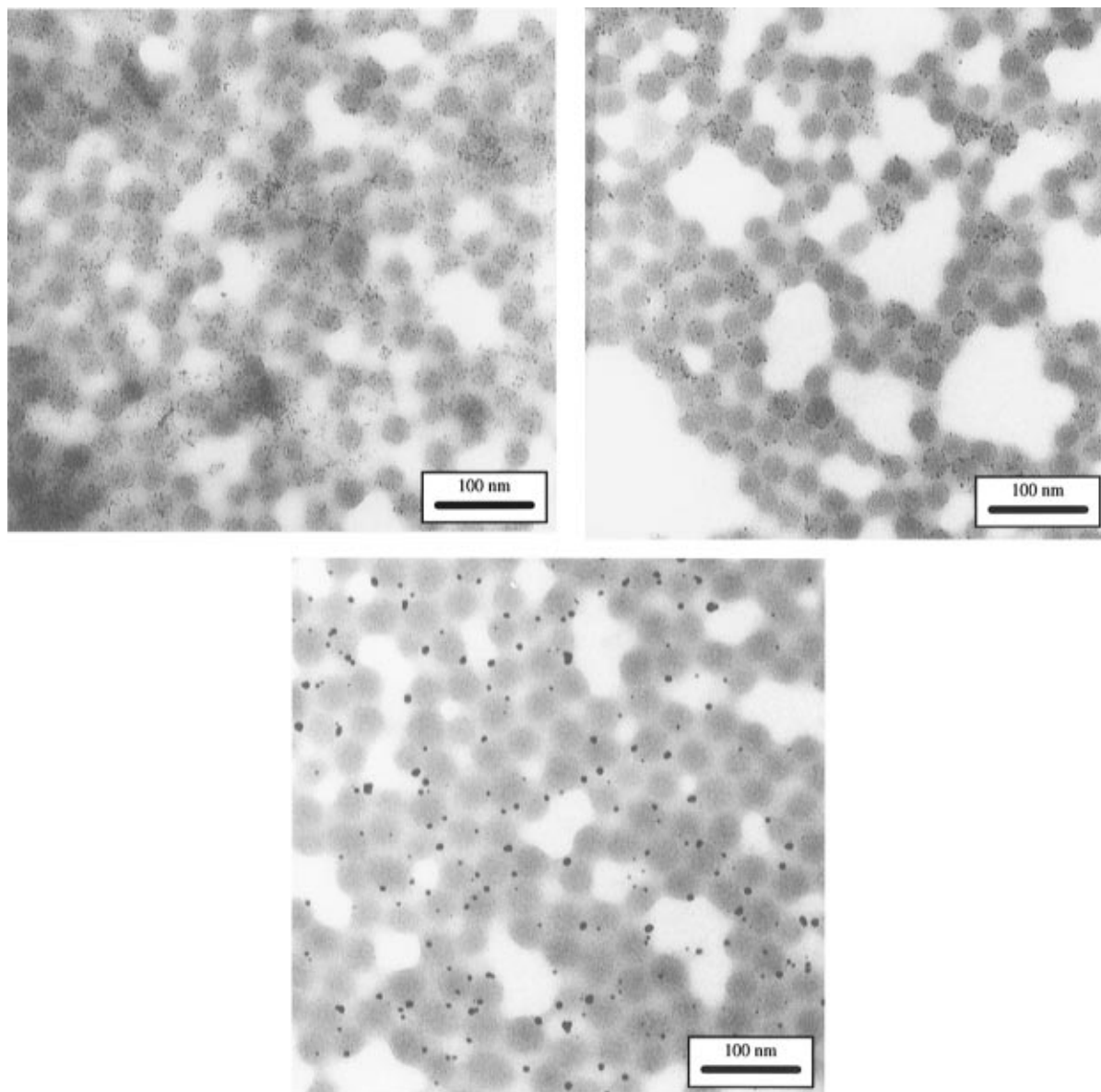
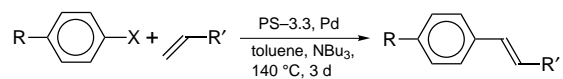


Figure 1. Transmission electron micrographs of Pd colloids in block copolymer micelles. In part a (top left) the solubilized Pd(OAc)₂ was reduced by “fresh” superhydride (very fast reduction) leading to many very small metal particles in the micelle core. The application of “old”, partially hydrolyzed superhydride under otherwise similar conditions (slower reduction) is leading to bigger particles (part b, top right). In part c (bottom), the Pd(OAc)₂ was reduced by bubbling hydrogen (slow reduction) leading to almost one big particle per micelle.

Table 2. Coupling of Olefins and Various Haloarenes in the Presence of PS-3.3, Pd^a



entry	R	R'	X	yield ^a [%]
1	-H	-C ₆ H ₅	Br	2
2	-CH ₃	-C ₆ H ₅	Br	7
3	-CF ₃	-C ₆ H ₅	Br	60
4	-F	-C ₆ H ₅	Br	4
5	-C(O)CH ₃	-C ₆ H ₅	Cl	0
6	-C(O)CH ₃	-C ₆ H ₅	Br	92 ^b
7	-C(O)CH ₃	-C(O)OC ₄ H ₉	Br	93 ^c
8	-NO ₂	-C ₆ H ₅	Br	92 ^d
9	-NO ₂	-C(O)OC ₄ H ₉	Br	99 ^e

^a GC yield. ^b After 2 days. ^c After 5 h; xylene as solvent. ^d After 1 day. ^e After 75 min; xylene as solvent. ^f Catalyst PS-3.3, Pd was 0.05 mol % related to the amount of haloarene.

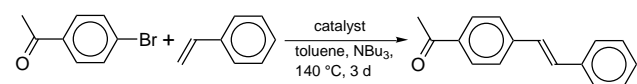
pyridyl ligands to accomplish educt conversion on an acceptable time scale which has been shown previously with other pyridyl

ligands.²⁶ Yields were low with nonactivated haloarenes (Table 2, entries 1–4), and no conversion was observed with chloroacetophenone (Table 2, entry 5). On the other hand, high product yields were obtained with bromoarenes substituted by electron withdrawing substituents and styrene or butylacrylate as the coupling component (Table 2, entries 6–9) as it is also known for the Heck reaction under standard conditions.²¹

In a second set of experiments, we employed a number of potential Pd catalysts for the couplings of 4-bromoacetophenone and styrene, using both diverse block copolymer stabilized colloids as well as classical catalysts. The comparison of different catalysts revealed considerable differences, as shown in Table 3.

The usage of low molecular weight Pd catalysts—in particular at high temperatures—may lead to the formation of “Pd-black” (weakly stabilized, ill defined Pd colloids), which is obviously also able to catalyze the coupling of olefins and haloarenes leading to moderate yields²¹ (Table 3, entry 1). Similar results

(26) Klingelhöfer, S. Ph.D. Thesis, Marburg, 1996.

Table 3. Coupling of Styrene and 4-Bromoacetophenone in the Presence of Different Catalyst Systems

entry	catalyst	Pd [mol %] ^a	yield [%] ^b
1	5% Pd/C	1	35
2	Pd(OAc) ₂	0.05	30
3	Pd(OAc) ₂ /TOP ^c	0.05	87
4	Pd(OAc) ₂ /pyridine ^d	0.05	76
5	Pd(OAc) ₂ /P4VP ^e	0.05	1
6	PS-3.3, Pd	0.5	78
7	PS-3.3, Pd	0.05	92 ^f
8	PS-3.3, Pd	0.005	73 ^g
9	PS-3.3, Pd	0.0012	68 ^h
10	PS-3.3, Pd	0.05	83 ^{ij}
11	PS-3.3, Pd	0.05	84 ^j
12	PS-7.1, Pd	0.05	75
13	PS-11.1 A, Pd	0.05	72
14	PS-11.1 B, Pd	0.05	3
15	PS-5.2, Pd	0.5	53
16	PS-5.2, Pd (20%)/Ni (80%)	0.5	63 ^g
17	PS-5.2, Ni (100%)	0.5	0 ^g

^a Related to 4-bromoacetophenone. ^b GC yield. ^c TOP:Pd = 6:1 (mol). ^d Pyridine:Pd = 1000 (mol). ^e PVP:Pd = 700 (mol). ^f After 2 days. ^g After 4 days. ^h After 5 days. ⁱ In DMF. ^j After 1 day.

were obtained with the precursor salt palladium acetate as catalyst (Table 3, entry 2).

As expected, product yields were increased significantly with Pd(OAc)₂/tri-*o*-tolylphosphine (TOP) (Table 3, entry 3). The successful use of (PS-3.3, Pd) as catalyst for Heck reactions implies that pyridine can be used instead of TOP as a ligand for Pd, which was confirmed in one experiment (Table 3, entry 4). It is worth mentioning that the usage of pyridine results in the same amount of product, but at lower reaction rates.

The cross-experiment of employing Pd(OAc)₂ in the presence of linear, nonblocked poly-4-vinylpyridine (P4VP) did result in almost zero product yield, which is obviously due to the insolubility of P4VP in toluene (Table 3, entry 5). The extremely poor product yields in comparison to the coupling with Pd(OAc)₂ as catalyst indicate that P4VP is an efficient reagent for the removal of Pd, which can be of interest for the preparation of catalyst free materials.

Block copolymer stabilized colloids were employed as catalysts under analogous reaction conditions (Table 3, entries 6–17). Their catalytic efficiencies depend significantly on the relative amount of Pd (to bromoacetophenone), on the micelle size, as well as on the dispersity and type of metal (Table 3). The catalytic activity of (PS-3.3, Pd) was at least as high as the activity of the standard Heck catalyst Pd(OAc)₂/TOP (Table 3, entry 3). Turnover numbers as high as 56600 mol of product/mol of catalyst were obtained with PS-3.3 (Table 3, entry 9), which certainly does not mark the upper limit since the reaction was simply stopped, and no formation of Pd-black or any precipitate was observed.

The catalytic reactivity of block copolymer stabilized palladium colloids significantly depends on the size of the stabilizing block copolymer micelles. Table 3 shows that Pd colloids stabilized by the smallest block copolymer (PS-3.3)—forming the smallest micelles with a diameter of 27 nm—show the best catalytic reactivity. On the other hand, palladium colloids stabilized by PS-5.2—the longest block copolymer with its micellar diameter of 64 nm—show less reactivity. All other polymers follow the same systematic trend (Table 3, entries 7 and 12–15).

There are two potential explanations for this difference in catalytic activity. The palladium colloids are localized in the micelle core (see Figure 1), and the educts have to diffuse through the micelle shell into the micelle core. Large block copolymer micelles are surrounded by longer polystyrene chains than are small micelles, which leads to more steric hindrance to the educts than for short polymer chains, and the reaction speed is decreased. Another reason for the higher reactivity of palladium colloids in small micelles is the larger specific surface of smaller micelles. It was shown that the core of PS-*b*-P4VP micelles has to be regarded as more or less solid.^{18,27} So, catalytic reactions have to take place in the interface region between core and shell (core surface). With decreasing micelle size, more specific core surface is produced, and more palladium particles are present at the core surface, thus resulting in a higher reactivity.

In one pair of experiments, we varied the size and dispersity of the palladium colloids inside the micelle cores by variation of the reduction conditions. “Fresh” superhydride (nonhydrolyzed LiB(C₂H₅)₃H) was used in the case of entry 13 in Table 3, whereas “old” superhydride (partially hydrolyzed LiB(C₂H₅)₃H) was used in the case of entry 14 in Table 3. The different morphologies of the resulting Pd colloids were already depicted in Figure 1, parts a and b. It turned out that an ultra-fine distribution of Pd in the micelle core is essential to obtain the described high reactivities: the slightly larger colloids produced with the “old” superhydride result in 3% conversion, only, whereas the correctly prepared catalyst possesses under similar conditions a conversion of 72%.

Pd(OAc)₂ containing block copolymer micelles which were not prerduced prior to reaction show similar low catalytic activities. Since Pd colloids are expected to be formed during the *in situ* reduction of Pd(OAc)₂ in the Heck reaction, this lower activity is related to a presumably more unfavorable particle size distribution of Pd in the micelle core, such as in the case of slow reduction processes as shown in Figure 1, parts b and c.

The comparison with the reference experiments with Pd black and Pd(OAc)₂ as catalysts for the Heck reaction underlines that all observed effects are due to the colloid morphology and the supporting shell of block copolymers. In contrast to common, classical colloidal noble metal catalysts, the presented system dissolves even in unpolar solvents like cyclohexane (above 35 °C), toluene, or THF. Due to the use of stabilizing block copolymers superior colloid stabilities even at high temperatures (140 °C) can be achieved. In contrast to palladium colloids stabilized by surfactants or chelating solvents, block copolymer stabilized metal colloids are not sensitive to aging.¹¹ Our colloidal solutions—stored under argon—remain active even after months.

Partial replacement of Pd(0) in the micelles by nickel did result in a decrease of the catalytic activity, but marks a promising way to cheaper bimetallic systems. Under the applied reaction conditions, pure nickel colloids do not catalyze the Heck reaction (Table 3, entries 16 and 17).

As expected, remarkable differences in the reaction kinetics were found with different educts, where the reaction rate depends on the reactivity of both coupling components. Two selected kinetic experiments are shown in Figures 2 and 3.

Nearly 29 h were necessary to accomplish quantitative conversion of bromoacetophenone and styrene at 140 °C with PS-3.3 as catalyst (0.05 mol %) in xylene (Figure 2). In contrast, quantitative conversion of 4-bromonitrobenzene and butylacrylate was found under analogous reaction conditions

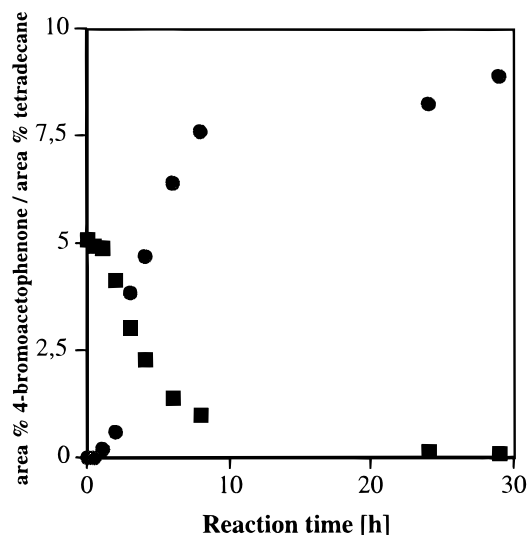


Figure 2. Plot of the area (percent) of 4-bromoacetophenone (■) and the area (percent) of product (●) versus reaction time for the coupling of bromoacetophenone and styrene at 140 °C in xylene with NBu_3 as base and with 0.05 mol % of the catalyst (PS-3.3, Pd), as obtained by GC analysis.

after 75 min (Figure 3). In both cases, we observe an induction period of about 30 min for the coupling of 4-bromonitrobenzene and butylacrylate. No formation of Pd-black was observed at the end of the reaction in both cases. The catalysts were reusable without any loss in activity.

Conclusion and Outlook

Hybrid colloids consisting of palladium colloids in the core of amphiphilic block copolymer micelles show a strong catalytic activity in the Heck reaction. The reactivities of these systems were compared with those of some low molecular complexes. The activity of the micellar stabilized colloids compares well with those of the standards, but at the same time, a much higher stability is found. The reactivities presented in Table 2 are just minimal values, since they only denote the number of active reaction cycles in a single batch reaction, i.e. the real TON-numbers in multiple use are significantly higher. The remarkable increased lifetime is regarded to be typical for colloidal catalysts, especially when they are embedded in the protecting cores of block copolymer micelles. In addition, adjustment of the outer, solvating block to the environment allows the Heck reaction to be performed in many "simple" solvents of choice, here toluene, instead of amidic solvents. Experiments in THF and cyclohexane were also performed and showed similar

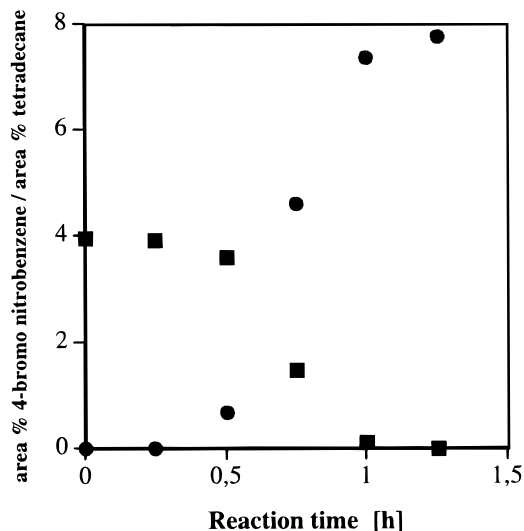


Figure 3. Plot of the area (percent) of 4-bromoacetophenone (■) and the area (percent) of product (●) versus reaction time for the coupling of 4-bromonitrobenzene and butylacrylate at 140 °C in xylene with NBu_3 as base and with 0.05 mol % of the catalyst (PS-3.3, Pd), as obtained by GC analysis.

results, but were not discussed in this paper. No formation of Pd black as a side product is observed, which is important for the use of the reaction products for pharmaceutical and electrooptical applications.

Considering these facts, the further development of block copolymer stabilized colloidal catalysts has promising perspectives. The limited reactivities toward nonactivated bromoarenes will certainly be overcome by tailor made block copolymers with modified, electron-donating ligands for Pd, which will also allow the coupling of chloroarenes instead of bromoarenes. This type of polymer stabilized Pd colloid will also have an impact on other metal catalyzed coupling reactions such as the Suzuki reaction, the Stille reaction, and Pd assisted carbonylation reactions.

Acknowledgment. The authors acknowledge financial support provided by the Deutsche Forschungsgemeinschaft and the Max Planck Society. S. Oestreich thanks the "Stiftung Stipendien-Fonds des Verbandes der Chemischen Industrie" for a Kekulé fellowship. We thank Uwe Justus for technical help during the experiments.

JA9714604