Conductive Polymers

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# Processing of Polyacetylene from Aqueous Nanoparticle Dispersions**

*Johannes Huber and Stefan Mecking**

Conjugated, conductive polymers are the key component in the development of flexible displays, low-cost, large-scale displays, and thin-film transistors.[1] However, ever since the seminal discovery of the conductive nature of ("doped") polyacetylene by Heeger, McDiarmid, Shirakawa, and coworkers, the processing of conductive polymers into devices has been a critical issue.[2–7] The rigid conjugated polymer backbone results in very low solubilities in organic solvents and thermal properties that prohibit thermoplastic processing. These drawbacks can be overcome to some extent by introducing substituents as side chains, which, however, also alters the electronic properties and often requires additional synthetic effort.[1] Polyacetylene itself is still considered unprocessable.[4–8] Grafting to other polymers has been reported to result in processable materials.[9–11] We report a different approach, namely, the synthesis of aqueous dispersions of submicron polyacetylene particles by catalytic polymerization in emulsion. Such dispersions are suited for processing by printing techniques, as exemplified by the generation of a polyacetylene-based functioning electronic circuit by ink-jet printing as a straightforward and versatile technique.

The concept of processing polyacetylene from polymer particle dispersions was suggested early on, but hitherto has not been reported.[12,13,38] The few examples of polyacetylene particle dispersions reported to date are restricted to dispersions of polyacetylene in organic solvents.[12,14,15] The reported catalyst productivities are very low (35 mol acetylene per mol metal),[15] such that metal residues can be problematic for polymer stability and also for the electronic properties. It is well known that polymer particles can be stabilized in aqueous dispersions effectively by appropriate surfactants. Printing techniques are usually developed for aqueous systems. The insolubility of most polymers in water can be advantageous in the preparation of multilayer devices, in which the application of organic solvents often poses

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[*] Dipl.-Chem. J. Huber, Prof. Dr. S. Mecking
Universität Konstanz
Lehrstuhl für Chemische Materialwissenschaft
Fachbereich Chemie
Universitätsstrasse 10, 78457 Konstanz (Germany)
Fax: (+49) 7531-88-5152
E-mail: stefan.mecking@uni-konstanz.de

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problems because of unwanted re-dissolution of already applied layers. For these reasons, we studied the approach of aqueous polyacetylene dispersions.

Aqueous polymer dispersions are traditionally prepared by free-radical routes.[16] However, the polymerization of acetylene is viable only catalytically. The sensitivity of catalysts towards water is a major issue for catalytic polymerizations in aqueous systems. The most common catalysts for insertion polymerization are based on early transition metals, most prominently complexes with $d^0$ metals such as titanium and zirconium. These complexes are highly oxophilic and very reactive towards water. By comparison, complexes of late transition metals, usually with $d^8$ metals, are softer Lewis acids and consequently less oxophilic.[9–11,17–20]

Cationic palladium diphosphine complexes are well known to copolymerize olefins with carbon monoxide by an insertion mechanism, and they have been noted to polymerize substituted acetylenes in non-aqueous systems.[21–24] However, in general, acetylene polymerization appears to be less viable than polymerization of substituted acetylenes in terms of catalysts suited and catalyst activity.[25–27] By studying different diphosphine-based catalysts, we found that a palladium(II) catalyst modified by 1,3-bis(di-*tert*-butyl)phosphinopropane (**1**)[28] is very active for the polymerization of acetylene in aqueous emulsion (Table 1).[29] To prepare a dispersion of small (submicron) particles, the initial reaction mixture including the hydrophobic catalyst must be highly disperse.[30–34] A mixture of **1** and $Pd(OAc)_2$ was dissolved in a small volume of hexane/ethanol, and mixed with an aqueous solution of sodium dodecylsulfate (SDS) surfactant and methane sulfonic acid.[35] Sonication of the mixture afforded a miniemulsion. Gentle stirring under an acetylene atmosphere at ambient pressure resulted in the formation of an intensely colored, black dispersion (Figure 1). TEM images (Figure 2) reveal unexpectedly small particle sizes of approximately 20 nm.

***Table 1:*** Synthesis of polyacetylene dispersions.[a]

| Entry | Pd [μmol] | Surfactant conc. [% w/w] | *T* [°C] | Reaction time [h] | Polymer solids content[b] [%] |
|---|---|---|---|---|---|
| 1 | 78 | 1.0 | 25 | 1 | 0.7 |
| 2 | 90 | 2.5 | 25 | 3 | 4.2 |
| 3 | 90 | 2.5 | 25 | 6 | 6.5 |
| 4 | 90 | 4.0 | 25 | 6 | 6.9 |
| 5 | 90 | 2.0 | 50 | 2 | 2.2 |

[a] $Pd(OAc)_2/tBu_2P(CH_2)_3PtBu_2 = 1{:}3$; surfactant: SDS; total volume: 40 mL (entries 2, 4), 50 mL (entries 1, 3, 5). [b] Polymer solids content only, emulsifier excluded.

A possible mechanism for the particle formation involves polymerization starting in the hexane miniemulsion droplets. As polyacetylene is highly insoluble, it should precipitate rapidly during polymerization to form particles, which may exit the droplets and stabilize themselves by adsorption of surfactant. If the active sites remain within the hexane droplets, particles could form continuously. This assumption is supported by the observation that polymerization continues for hours, even though swelling of existing particles with monomer should be very low. Although speculative at this point, this mechanism would account for the unusually small particle sizes observed (much smaller than miniemulsion droplets).

***Figure 1.*** Appearance of a polyacetylene dispersion (polymer solids content 6.4 %). Left to right: undiluted, $10^3$-, $10^4$-, and $10^5$-fold dilution.

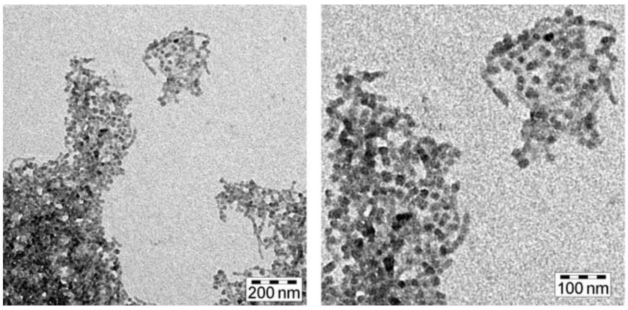

***Figure 2.*** TEM images of polyacetylene particles (entry 3 in Table 1).

Optimization of the catalyst loading, surfactant concentration, and reaction time afforded dispersions with polyacetylene solids contents of 7 % w/w (Table 1). Catalyst productivities correspond to $1.4 \times 10^3$ mol acetylene per mol Pd. Drawing samples from an ongoing reaction revealed the catalyst to be active for more than six hours in aqueous emulsion (see the Supporting Information).

No difference in polymer yield was observed when acetylene was polymerized as received (99 %, delivered as a solution in acetone adsorbed in diatomaceous earth) or purified by various methods (passage through concentrated sulfuric acid and activated carbon), which reveals that the catalyst is rather insensitive to monomer purity.

IR spectroscopy on the isolated bulk polymer reveals the material to contain a mixture of *cis* and *trans* repeat units (60:40). Tempering at 120 °C results in complete conversion to the *trans* structure, as reported previously for polyacetylene prepared with Shirakawa-type catalysts.[36]

Continuous films with a metallic luster could be obtained on various substrates, such as glass and paper, by simple dip-coating or spreading of dispersions on the substrate and subsequent drying (Figure 3). The films on paper are flexible and stable against dynamic bending. An average thickness of 0.7 μm was determined from the weight of the dispersion applied for a film prepared by spreading of a dispersion on high-gloss ink-jet paper and drying in warm air. After doping the film with iodine, the conductivity was found to be approximately $50\,S\,cm^{-1}$. Reported conductivities of bulk

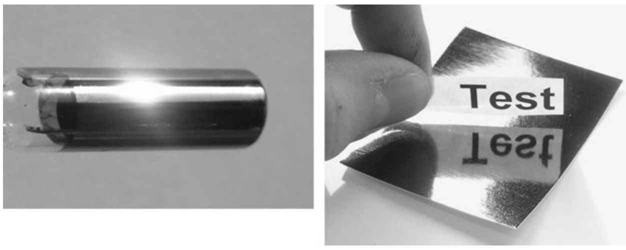

**Figure 3.** Polyacetylene film on glass formed by dip-coating into a dispersion (left), and film obtained by spreading on paper (right; smooth-surfaced paper for photo printing used).

polyacetylene vary considerably and are influenced by orientation induced by stretching and by the doping procedure. Values range from $10^2$ to $10^5$ S cm$^{-1}$.[3,6,37] In our films, the surfactant shell and possibly voids in the film may influence the conductivity. Polyacetylene is generally considered to be unstable in air.[4–6] Therefore, the conductivity of the films in air was measured over time. A decrease of conductivity to one fifth of the initial value was observed after 48 h. This result demonstrates a limited, but rather surprising, stability of the doped material in air, which is sufficient for the studies reported herein.

As a probe for facile processing into functional devices, the polyacetylene dispersions were printed by means of a commercial ink-jet printer. Dispersions were used as obtained with the addition of 5 % v/v glycerol to adjust the drying rate. The printed films had an average thickness of around $10^2$ nm. The circuit depicted in Figure 4 was printed on plain paper and subsequently doped. The polyacetylene circuit also fulfills the function of a resistor in this case. Upon contacting one of the comb-shaped “keypads” with a finger, the resistance between the two connectors of the board (C1, C2) drops to between $10^5$ and $10^6$ $\Omega$, depending on the length of the circuit path (R1 to R10) of the individual key. The resistance can be translated into a tone by an appropriate circuit (see the Supporting Information), which allows simple tunes to be played.

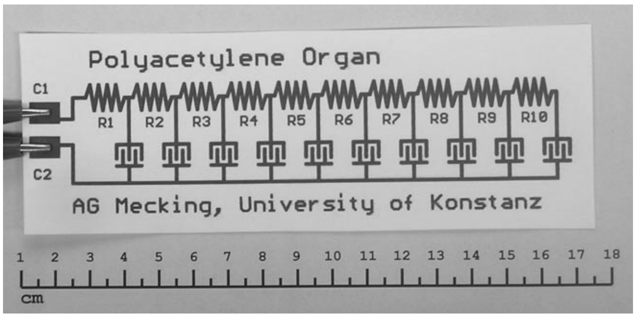

**Figure 4.** Ink-jet printed functional circuit board.

In summary, we have demonstrated the facile processing of polyacetylene from aqueous dispersions of submicron particles. As an example, ink-jet printing provides functioning circuits composed of this conductive polymer, which is widely considered unprocessable. The key step that enables access to the required dispersions is catalytic polymerization in an aqueous emulsion, with a suitable late-transition-metal catalyst. This approach is also of interest for other conjugated hydrocarbon-backbone polymers, such as polyparaphenylenes or polyphenylenevinylidenes.

## Experimental Section

Catalyst solution: Solutions of $Pd(OAc)_2$ (22.6 mg, 100 μmol) in acetonitrile (5 mL) and **1**[28] (99.7 mg, 300 μmol) in ethanol (5 mL) were mixed, and the solvent was evaporated in vacuo. The residue was dissolved in a mixture of ethanol (0.2 mL) and hexane (4.8 mL) to afford a catalyst solution with a concentration of 20 μmol Pd mL$^{-1}$. Solutions with up to 100 μmol Pd mL$^{-1}$ were prepared in this fashion.

Polymerization procedure: A mixture of an aqueous solution (50 mL) of SDS (1.25 g), a drop of methane sulfonic acid, and catalyst solution (1.5 mL, 90 μmol Pd) was sonicated for 2 min in a 100-mL round-bottom Schlenk flask closed with a septum (Bandelin HD 2200 with a KE76 tip, operated at 120 W). The septum was replaced by a connector with a tube to a bubbler. Acetylene was gently streamed over the solution via the Schlenk stopcock under stirring for six hours.

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