

# Communications to the Editor

## Nanoparticles from Step-Growth Coordination Polymerization

Johannes Pecher and Stefan Mecking\*

Fachbereich Chemie, Universität Konstanz, Universitätsstr. 10, D-78457 Konstanz, Germany

Polymer nanoparticles have been studied intensely from a fundamental as well as applications oriented perspective.<sup>1</sup> They are prepared most often by free-radical polymerization in a nonsolvent for the polymer, usually water. In recent years, nonradical polymerization routes to aqueous polymer nanoparticle dispersions have found increased interest.<sup>2,3</sup> Coordination polymerizations in emulsion can offer access to nanoparticles of polymers with microstructures inaccessible by other polymerization mechanisms. A prerequisite is sufficiently water-insensitive catalysts. To date, these catalytic nanoparticle syntheses have been restricted to chain-growth polymerizations.<sup>3</sup> Step-growth polymerizations are much slower, and the metal site leaves the growing chain after each addition of a repeat unit, such that a prolonged stability toward water of the metal species occurring during polymerization appears a necessity.

Our interest in the latter reactions resulted from studies of conjugated polymer nanoparticles. Conjugated polymers can provide properties such as fluorescence, electroluminescence, or electrical conductivity.<sup>4</sup> They are key components for the development of, e.g., flexible displays, low-cost displays, or organic photovoltaics. Dispersions of conjugated polymer nanoparticles can contribute to resolve the notorious issue of processing of conjugated polymers, and they can improve control of composition of conjugated polymer blends on the nanoscale.<sup>5</sup>

Poly(phenylenevinylenes) (PPV) are probably the most widely studied class of conjugated polymers.<sup>6</sup> Numerous routes to their

Scheme 1. ADMET Polycondensation in Aqueous Emulsion

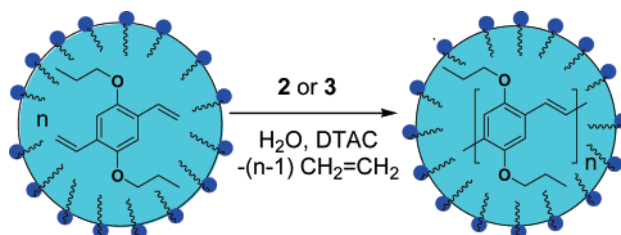


Table 1. Polymerization of 1,4-Dipropoxy-2,5-divinylbenzene (1) with Catalyst Precursors 2 and 3 in Toluene<sup>a</sup>

| entry | cat. | monomer/<br>catalyst | <i>t</i> (h) | $M_n \times 10^3$<br>(g mol <sup>-1</sup> ) <sup>b</sup> | yield (%) <sup>c</sup> |
|-------|------|----------------------|--------------|--|------------------------|
| 1     | 2    | 30                   | 24           | 2.2  | 60                     |
| 2     | 3    | 30                   | 24           | 2.8  | >95                    |
| 3     | 3    | 60                   | 24           | 2.0  | 84                     |
| 4     | 3    | 120                  | 24           | 1.5  | 77                     |
| 5     | 3    | 60                   | 72           | 2.4  | >95                    |

<sup>a</sup> 300  $\mu$ mol of **1**; 1 mL of toluene; 50 °C; reduced pressure: 750 mbar; quenched with excess ethyl vinyl ether. <sup>b</sup> From <sup>1</sup>H NMR spectroscopic quantification of end groups. <sup>c</sup> Isolated yield, obtained after workup by precipitation in methanol. In this procedure, any unreacted monomer would be removed (and also low oligomers to some extent).

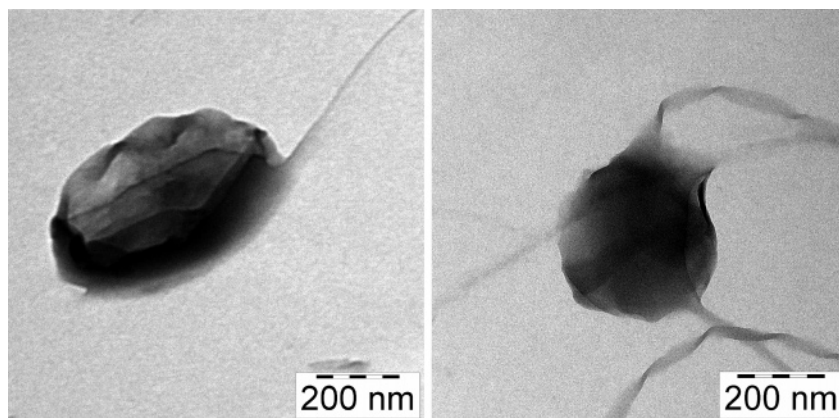
Table 2. Polymerization of 1 in Emulsion<sup>a</sup>

| entry | cat. | <i>t</i> (h) | $M_n \times 10^3$<br>(g mol <sup>-1</sup> ) <sup>b</sup> | yield (%) <sup>c</sup> | particle<br>size <sup>d</sup> (nm) |
|-------|------|--------------|--|------------------------|------------------------------------|
| 1     | 2    | 24           | 1.1  | 56                     | 300                                |
| 2     | 3    | 24           | 1.3  | 68                     | 210                                |
| 3     | 3    | 168          | 1.5  | 80                     | 230                                |

<sup>a</sup> Monomer/Ru = 100 molar ratio; *n*(Ru) = 10  $\mu$ mol; 1.5 mL of toluene; 300 mg of DTAC; 30 mL of water; 2 min ultrasound (120 W); 50 °C; reduced pressure: 750 mbar. <sup>b</sup> From <sup>1</sup>H NMR spectroscopic quantification of end groups. <sup>c</sup> Isolated yield, obtained after workup by precipitation of an aliquot of dispersion in methanol. In this procedure, surfactant and any unreacted monomer would be removed (and also low oligomers to some extent). <sup>d</sup> Volume average particle size determined by DLS.

synthesis have been elaborated.<sup>7–9</sup> These are based on post-polymerization reactions of precursor polymers<sup>7</sup> or direct polymerization to PPVs by various methods.<sup>8,9</sup> The latter include olefin metathesis reactions.<sup>9</sup> These require only a single

\* Corresponding author. E-mail: stefan.mecking@uni-konstanz.de.



**Figure 1.** TEM images of nanoparticles.

component as a starting compound and form few or no side products. Chain-growth ROMP of [2.2]paracyclophane-1,9-diene affords PPV with regularly alternating *cis*- and *trans*-vinylene linkages.<sup>9e,f</sup> Step-growth acyclic diene metathesis (ADMET) polycondensation of *p*-divinylbenzenes results in defect-free materials that possess all-*trans*-vinylene units.<sup>9a,b</sup>

In ADMET polycondensation by Ru alkylidenes, a ruthenium methylidene occurs as an active species, which is formed after each growth step. Ruthenium methylidenes are particularly susceptible toward decomposition by water.<sup>10,11</sup> For ADMET polycondensation it is advised that even trace water should be excluded carefully.<sup>12</sup>

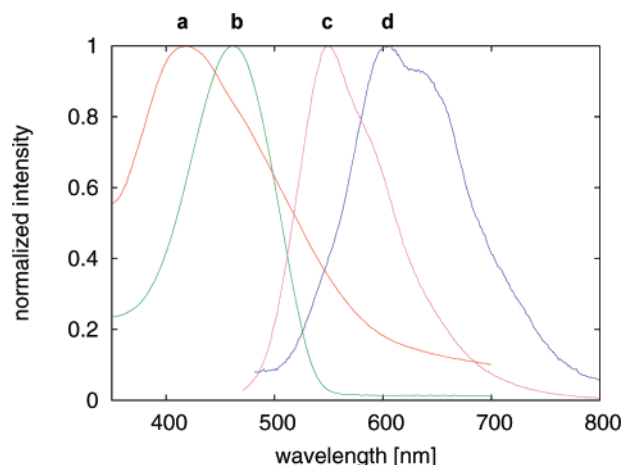
We report on the step-growth metathesis polymerization of 1,4-dipropoxy-2,5-divinylbenzene (**1**) in aqueous emulsion to afford PPV nanoparticles (Scheme 1).

Polymerization of **1** was studied initially in homogeneous organic phase. [(PCy<sub>3</sub>)(*η*-C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>Mes<sub>2</sub>)Cl<sub>2</sub>Ru=CHPh] (**2**, “Grubbs second generation”), which has been utilized previously in ADMET of divinylbenzenes,<sup>9c,d</sup> and [(*η*-C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>Mes<sub>2</sub>){κ<sup>2</sup>-=CH-*o*-(<sup>*i*</sup>PrO)C<sub>6</sub>H<sub>4</sub>}RuCl<sub>2</sub>] (**3**, “Hoveyda–Grubbs second generation”) were studied as catalyst precursors (Table 1). **3** was found to afford much higher conversions and higher polymer molecular weights (entries 1 and 2). Reducing the catalyst loading resulted in a decrease of polymer molecular weights and yields (entries 2 to 4). This indicates that under these conditions molecular weights are not limited by the unreactive end groups originating from the (monofunctional) aryl–alkylidene moiety of the catalyst precursor **3** (vide infra), but rather to limited conversion due to a slow reaction. Increased reaction time resulted in a substantially increased yield and somewhat higher molecular weight (entries 3 and 5).

Preliminary NMR studies confirm an efficient activation of **3** in this ADMET reaction. A toluene-*d*<sub>8</sub> solution of **3** and **1** (5 equiv) was warmed from –60 to 25 °C, monitoring the reaction by <sup>1</sup>H NMR spectroscopy. The Ru=CH– resonance of **3** at δ 16.57 ppm decreases and disappears, while a new signal at δ 16.30 arises, assigned to Ru=CH-[*p*-{2,5-(<sup>*n*</sup>PrO)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>}-CH=CHR)] (R = H or polymer chain).

For the polymerization of **1** in aqueous emulsions, concentrated toluene solutions of the catalyst precursor, and of the monomer, were mixed with an aqueous surfactant solution and miniemulsified by high shear generated by ultrasound. At 50 °C and slightly reduced pressure to facilitate removal of ethylene, polycondensation occurred to afford bright red nanoparticle dispersions (Table 2).

The cationic surfactant dodecyltrimethylammonium chloride (DTAC) was found to be compatible with the catalyst and suited for colloidal stabilization of the nanoparticles formed. By



**Figure 2.** Normalized absorption spectra and photoluminescence spectra of aqueous nanoparticle dispersions (a, d) and of poly-**1** in chloroform solution (*c* = 0.5 mg L<sup>-1</sup>; b, c).

contrast, no polymerization occurred in the presence of the anionic sodium dodecyl sulfate (SDS) with either **2** or **3**.<sup>13</sup> Lower polymer yields and molecular weights by comparison to the polycondensations in nonaqueous systems (Table 1) under otherwise similar conditions in terms of concentrations of reagents in the organic phase, temperature, and pressure may be attributed to partial catalyst decomposition. However, an increased reaction time resulted in some increase in polymer yield and molecular weight, confirming that a part of the catalyst remains active for prolonged periods of time (entries 2 and 3).

MALDI-TOF mass spectrometry analysis of poly-**1** (prepared in emulsion or in homogeneous nonaqueous polymerizations) confirms that the polymer chains possess two vinyl end groups (H<sub>2</sub>C=CH-[*p*-{2,5-(<sup>*n*</sup>PrO)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>}-CH=CH-]<sub>*n*</sub>H; cf. Supporting Information). In addition, a small portion of chains containing one end group originating from the catalyst precursor (**3**) is also observable in some samples. (2-(<sup>*i*</sup>PrO)C<sub>6</sub>H<sub>4</sub>-HC=CH-[*p*-{2,5-(<sup>*n*</sup>PrO)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>}-CH=CH-]<sub>*n*</sub>H). Cycles are not observed within experimental error.

Transmission electron microscopy (TEM) images of typical particles are depicted in Figure 1. In addition to isolated particles, many particles are also observed from which fiberlike structures originate. These appear helically twisted. PPV prepared by a postpolymerization synthesis from a polymeric precursor is known to possess a fibrillar structure, with a diameter of a few tens of nanometers.<sup>14</sup> The observed fiberlike structures can be assigned tentatively as poly-**1** fibers.

UV–vis absorption and fluorescence spectra of poly-**1** particle dispersions are given in Figure 2. By comparison to chloroform

solutions of the isolated polymer, the absorption maximum is significantly blue-shifted, and a red tail is observed. This is in accordance with observations on a related PPV,<sup>15</sup> which have been attributed to reduced conjugation length and increased intrachain interactions in the particles. Similar fluorescence spectra are observed for the particle dispersions and for thin films prepared from the dispersions by spin-coating (cf. Supporting Information). A large Stokes shift is observed, which is commonly attributed to energy transfer to low-energy chromophores and weakly fluorescent aggregates.<sup>16</sup>

Lateral structures of poly-**1** were obtained by simple ink-jet printing of the particle dispersions (Supporting Information).

In summary, ADMET polycondensations can be carried out in aqueous systems. We have demonstrated the synthesis of polymer nanoparticles by a step-growth coordination polymerization, in the form of aqueous dispersions, for the first time. Fluorescent dispersions of PPV nanoparticles are obtained. We are currently studying their potential for the facile processing of conjugated polymers to organic light-emitting devices.

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**Supporting Information Available:** Experimental procedures, NMR spectra of poly-**1** and of reaction of **3** with **1**, MALDI-TOF, and additional fluorescence spectra; additional images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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