

**POLY(*p*-PHENYLENE VINYLENE) NANOPARTICLES BY
ACYCLIC DIENE METATHESIS (ADMET) POLYCONDENSATION
IN AQUEOUS EMULSION**

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Introduction

Poly(*p*-phenylene vinylene) (PPV) and its derivatives are amongst the most widely studied class of conjugated polymers since the discovery of their electroluminescent properties in 1990.¹ These polymers are studied for applications in numerous photonic devices such as organic solar cells, organic light emitting diodes (OLEDs), but also in field-effect transistors and electrochemical cells.^{2,3} Nanoparticles of conjugated polymers may contribute to resolve the manifest issue of processing this class of polymers.

Aqueous polymer dispersions are of interest in this context, as printing techniques are compatible with aqueous systems, and water is a non-solvent for most polymers. Beyond the traditional free-radical emulsion polymerization applied industrially, catalytic polymerization in aqueous emulsion has evolved as a general route to polymer nanoparticle dispersions. However, a prerequisite are sufficiently water-insensitive catalysts.

Numerous synthetic routes towards PPV have been elaborated. Post-polymerization of precursor polymers⁴⁻⁶ or direct polymerization to PPVs by various methods,^{7,8} including olefin metathesis reactions,⁹⁻¹³ have been reported. The facile availability of monomers and the marginal occurrence of side products and defects makes olefin metathesis a useful synthetic tool in PPV synthesis. PPV with regularly alternating *cis*- and *trans*-vinylene linkages can be accessed by chain-growth ROMP of [2.2]paracyclophane-1,9-diene.¹³ Step-growth acyclic diene metathesis (ADMET) polycondensation of *p*-divinylbenzenes results in defect-free materials bearing all-*trans*-vinylene units.^{9,10}

Recently, we demonstrated the ADMET polycondensation of 1,4-dipropoxy-2,5-divinylbenzene in aqueous emulsion with Ru alkylidene catalysts affording PPV nanoparticles as a bright red latex.¹⁴ In step-growth polymerizations, the catalyst leaves the polymer chain after each addition of a repeat unit, making the active species particularly susceptible towards water.

The active metal site is stabilized by chelating κ -O coordination of the alkoxy moiety in alkylidene species formed from the monomer, similar to the coordination environment in the robust and moisture-insensitive catalyst precursor **2**. A small portion of the water-sensitive catalyst remains active for several days.

We report the step-growth metathesis polymerization of 1,4-dialkyl-substituted divinylbenzene by Ru metathesis catalysts in aqueous emulsion to afford PPV nanoparticles. [(PCy₃)(η -C₃H₄N₂Me₂)Cl₂Ru=CHPh] (**1**, "Grubbs second generation") and [η -C₃H₄N₂Me₂]{ κ -C=CH-*o*-(*PrO*)C₆H₄}RuCl₂] (**2**, "Hoveyda-Grubbs second generation") were employed as catalyst precursors for the ADMET polycondensation of 1,4-bis(2'-ethylhexyl)-2,5-divinylbenzene (**3**). Additional polymerizations were carried out in homogeneous organic phase for comparison.

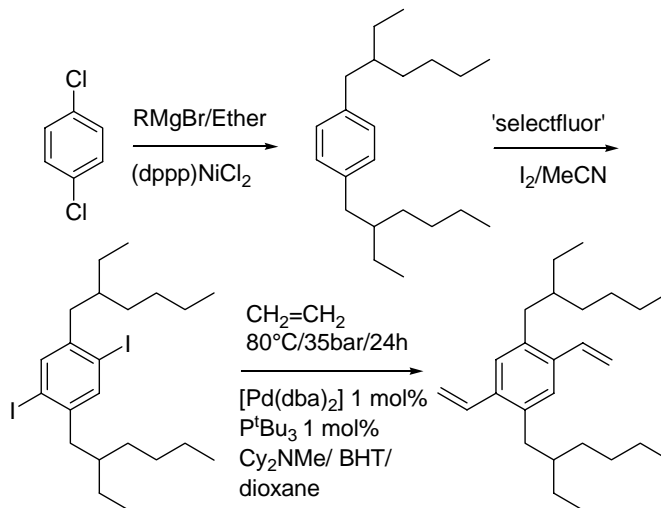
Experimental

Monomer Synthesis. 1,4-bis(2'-ethylhexyl)-2,5-divinylbenzene (**3**) was synthesized in three steps starting from 1,4-dichlorobenzene (Scheme 1). A standard *Kumada*-coupling afforded 1,4-bis(2'-ethylhexyl)benzene, which was ortho-iodinated with iodine and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor[®]) in acetonitrile.¹⁵ A subsequent *Heck*-reaction with ethylene afforded **3**. All intermediates were purified either by distillation or column chromatography and characterized by NMR. GC-MS revealed a purity of **3** of ca. 95% with some mono-vinyl substituted product as an impurity.

Emulsion Polymerization. All manipulations of ruthenium complexes were carried out under an inert atmosphere using standard glovebox or Schlenk techniques. Monomer and catalyst precursor were separately dissolved in dry toluene and injected into an aqueous surfactant solution (1 wt.-%), and immediately miniemulsified by high shear generated by ultrasound (120W). Polycondensation was carried out at 50 °C and slightly reduced pressure (750 mbar) to shift the equilibrium by ethylene removal. After 24 h, the emulsion was cooled to room temperature, quenched with ethyl vinyl ether and stirred open to air for 24 h to remove toluene by evaporation. An aliquot of the greenish latex obtained was precipitated in methanol to

isolate and characterize the polymer by NMR and GPC. In this procedure, surfactant and any unreacted monomer would be removed (and also low oligomers to some extent). TEM and DLS were employed to determine particle sizes. M_n was determined by ¹H NMR spectroscopic quantification of end groups and verified by GPC.

Homogeneous Polymerization. Monomer and catalyst were dissolved separately in dry toluene. The two solutions were combined and heated to 50 °C at reduced pressure (750 mbar) for 24 h (Table 1). The reaction mixture was cooled to room temperature, quenched with excess ethyl vinyl ether, and the polymer was precipitated in cold methanol as a yellow solid. The isolated materials were dried under high vacuum and characterized by NMR spectroscopy and GPC.



Scheme 1. Synthesis of 1,4-bis(2'-ethylhexyl)-2,5-divinylbenzene (**3**).

Results and Discussion

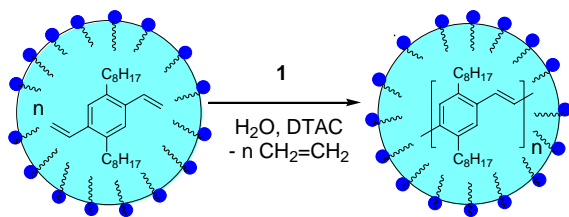
Polymerization of the dialkyl substituted divinylbenzene **3** in homogeneous organic phase is possible with both catalyst precursors, with comparable conversions and molecular weights (Table 1).

Table 1. Polymerization Of 1,4-Bis(2'-Ethylhexyl)-2,5-Divinylbenzene (**3**) With Catalyst Precursors **1** And **2** In Toluene

entry	catalyst precursor	monomer/catalyst	M _n × 10 ³ (g mol ⁻¹) ^a	yield (%)
1	1	30	3.3	50
2	1	60	3.0	84
3	2	30	4.2	40
4	2	60	4.2	79

^a From ¹H NMR spectroscopic quantification of end groups.

¹H NMR spectroscopy of the isolated polymers revealed vinyl end groups, indicating that the molecular weights are not limited by the monofunctional alkylidene unity introduced with the catalyst precursor, or monofunctional impurities in the monomer (cf. experimental section). This is further supported by the observation that increased reaction times > 24 h resulted in higher molecular weights up to 10⁴ g mol⁻¹. In contrast, in the ADMET polycondensation of the corresponding dialkoxy substituted monomer 1,4-bis[(2'-ethylhexyl)oxy]-2,5-divinylbenzene (**4**) catalyst precursor **2** was more productive than **1** (data not shown). These observations can be rationalized by the assumption that the phosphine ligand introduced with catalyst precursor **1** can retard polymerization by blocking a coordination site, but also stabilizes intermittently occurring unsaturated species. For **2**, lacking the phosphine, unsaturated species can be stabilized by chelating κ -O coordination of the alkoxy substituents in the case of polymerization of **4**, but not in the case of the alkyl-substituted monomer **3**.



Scheme 2. ADMET polycondensation of **3** in aqueous emulsion.

The polymerization of **3** in aqueous emulsion with catalyst precursor **1** afforded a fluorescent light green colloiddally stable polymer latex of 110 nm volume average particle size (Scheme 2). GPC revealed the molecular weight of the isolated polymer to be $1.7 \times 10^3 \text{ g mol}^{-1}$. With catalyst precursor **2**, the reaction mixture turned grey within a few hours and no polymer could be isolated, indicating catalyst decomposition. Under the conditions studied, catalyst **2** seems to be unstable when polymerizing dialkyl substituted divinylbenzenes in emulsion. In contrast, emulsion polymerization of dialkoxy substituted monomers is possible with both catalysts **1** and **2**, the latter resulting in higher molecular weights and higher yields.¹⁴ This again underlines the assumption that the alkoxy substituents introduced with the monomer have an essential stabilizing effect in the catalyst resting state.

Conclusions

In summary, fluorescent nanoparticle dispersions of a dialkyl substituted poly(*p*-phenylene vinylene) can be prepared via ADMET polycondensation in aqueous emulsion with catalyst precursor **1**. The possibility of polymerizing dialkyl-substituted divinylbenzenes, which do not bear alkoxy groups capable of coordination to the metal center resulting in stabilization of the catalyst, in aqueous emulsion suggests the feasibility of the synthesis of unsubstituted PPV in a similar procedure. First attempts with *p*-divinylbenzene confirmed the higher activity of **1** (60 % yield) compared to **2** (15 % yield).

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