

# EMULSION POLYMERIZATION OF BUTADIENE WITH A CATIONIC NICKEL CATALYST

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## Introduction

Polymer dispersions are produced on a large scale, e.g. for coatings and paints. They are usually manufactured by free-radical emulsion polymerization. One of the major monomers is butadiene (BD), which is readily available from cracking of hydrocarbon feedstocks.

The versatility of butadiene insertion (1,2, 1,4-*trans*, or 1,4-*cis*) in principle allows for the synthesis of polymers with various and controlled microstructures and therefore very different materials. However, by free-radical polymerization polybutadiene (PBD) dispersions with only a very limited range of microstructures are accessible. BD is typically incorporated as 14 % *cis*-1,4; 69 % *trans*-1,4 and 17 % 1,2- (*vinyl*) units.<sup>1</sup> Coordination polymerization can allow for a much broader microstructure control.<sup>2</sup> Cationic nickel(II) complexes are known to polymerize butadiene in organic solvents. 1,2-incorporation is low and the *cis/trans* ratio depends on the nature of the coordinating ligand and the counterion.<sup>3</sup>

## Experimental

**Synthesis of catalyst precursor (1).** In a Schlenk flask, 108 mg (0.4 mmol) [(allyl)NiCl]<sub>2</sub>, 572 mg (1.62 mmol) SbPh<sub>3</sub>, and 718 mg (0.81 mmol) NaBAR<sup>F</sup><sub>4</sub> (Ar<sup>F</sup> = 3,5-(CF<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>)<sup>4</sup> were combined. At -60°C, 10 mL of cold diethyl ether were added and the dark red solution was stirred for 2 h while slowly warming to room temperature. The solvent was removed under vacuum. The residue was dissolved in 10 mL of dichloromethane and filtered over a pad of celite. The solvent was removed in vacuum, and the solid residue was washed twice with 10 mL of pentane. **1** is obtained as a brown powder in 91% yield (1215 mg). Crystalline material can be obtained from a CH<sub>2</sub>Cl<sub>2</sub> solution by addition of pentane. All manipulations of the complex including the polymerizations were carried out under an inert atmosphere.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C): 2.97 (d, 2 H, H<sub>anti</sub>, <sup>3</sup>J = 14 Hz), 4.57 (d, 2 H, H<sub>syn</sub>, <sup>3</sup>J = 7 Hz), 5.52 (tt, 1 H, H<sub>syn</sub>, <sup>3</sup>J = 14 Hz, <sup>2</sup>J = 7 Hz), 7.18 (m, 12 H), 7.29 (m, 12 H), 7.43 (m, 6 H), 7.54 (s, 4 H, BAR<sup>F</sup>), 7.71 (s, 8 H, BAR<sup>F</sup>). Anal. calcd. for C<sub>71</sub>H<sub>47</sub>BF<sub>24</sub>NiSb<sub>2</sub> (M = 1669,1 g mol<sup>-1</sup>): C 51.09 %, H 2.84 %. Found: C 51.18 %, H 2.90 %.

**Polymerization Procedure.** 2.25 g of SDS were dissolved in 300 mL of degassed water and transferred to a nitrogen-purged 500 mL glass pressure reactor equipped with a mechanical stirrer and a heating/cooling jacket (set to 20°C initially) controlled by a thermocouple dipping in the reaction mixture. **1** was dispersed in a mixture of 12 mL of toluene and 0.6 mL of hexadecane, and transferred into the reactor. Under stirring (500 rpm) butadiene was added and ultrasound (150 W, 2 min) was applied immediately by means of a sonotrode installed in the reactor. The temperature was set to 25°C. After 4 h the polymerization was stopped by releasing the residual pressure, evacuating, and exposing to air. For analysis of the bulk polymer an aliquot of the latex was precipitated with methanol containing BHT. The supernatant solvents were filtered off, the polymer was washed with methanol and dried over night at 50°C under vacuum.

## Results and Discussion

The lipophilic cationic Ni(II) allyl complex [(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)Ni(SbPh<sub>3</sub>)<sub>2</sub>][BAR<sup>F</sup><sub>4</sub>] (**1**) was prepared in a one-pot reaction from dimeric nickel allyl chloride, SbPh<sub>3</sub>, and NaBAR<sup>F</sup>.

To prepare polymer emulsions, a high degree of dispersion of the catalyst in the initial reaction mixture is a prerequisite. For lipophilic catalyst precursors, this can be obtained in the form of aqueous miniemulsions of solutions of the catalyst precursor in a small amount of organic solvent, or monomer.<sup>5</sup> For butadiene polymerization with **1** in aqueous emulsion, an incomplete solubility of **1** in the (organic phase of the) initial reaction mixture was found to be mandatory. No polymerization activity was observed under conditions where **1** was completely soluble. Presumably, the catalyst is somewhat sensitive towards water. In an undissolved state the precatalyst endures sonication. Once the miniemulsion droplets are generated, the

complex slowly dissolves as polymerization starts and the lipophilic butadiene chain grows on the metal center, the active species now being protected towards water by BD and polybutadiene (PBD). **Table 1** gives selected polymerization results. In all cases stable latices were obtained. Transmission electron microscopy (**Figure 1**) reveals spherical particles up to ca. 200 nm in diameter. Catalyst productivities up to TON = 1.5 × 10<sup>3</sup> mol(BD)/mol(Ni) were observed (e.g. entry 1). Complete conversion of the monomer could be achieved (entry 2). Additional monomer could also be added to the ongoing polymerization (entry 4; second BD batch added after 30 min) without negative effects on colloidal stability.

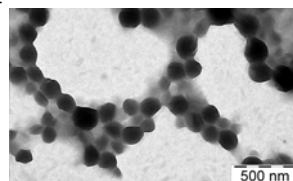
**Table 1. Emulsion Polymerization of Butadiene with Precatalyst 1**

no	cat.	BD	PBD (conversion)	TON	M <sub>n</sub> (M <sub>w</sub> /M <sub>n</sub> ) <sup>a</sup>	vinyl/cis/ trans <sup>b</sup>	T <sub>tr</sub> , T <sub>m</sub> <sup>c</sup>
1	150 μmol	26 g	12.5 g (48%)	1.5 × 10 <sup>3</sup>	3.1 × 10 <sup>4</sup> (3.1)	4/23/73	47, 69
2	300 μmol	15 g	15.0 g (100%)	0.9 × 10 <sup>3</sup>	2.3 × 10 <sup>4</sup> (7.9)	5/17/78	48, 74
3	150 μmol	27 g	22.6 g (84%)	1.4 × 10 <sup>3</sup>	3.4 × 10 <sup>4</sup> (4.7)	4/18/78	48, 77
4	300 μmol	9.4+ 13 g	12.5 g (56%)	1.5 × 10 <sup>3</sup>	3.0 × 10 <sup>4</sup> (3.4)	4/18/78	48, 73

reaction conditions: 300 mL of water, 2.25 g of SDS, 25 °C, 4 h. a): from GPC vs. PS standards. b) determined by IR spectroscopy. c) T<sub>tr</sub>: temperature of the monoclinic-hexagonal phase transition [°C]; T<sub>m</sub>: melting point [°C].

In organic solvents, similar complexes are known to produce high *cis*-PBD.<sup>3</sup> This was also observed in polymerizations with **1** in organic solvents (*vinyl/cis/trans* = 4/90/6). In the aforementioned experiments in aqueous emulsion, butadiene is predominantly incorporated in a *trans* fashion. A free-radical mechanism can be excluded, amongst others from the microstructure, namely the low 1,2-content. Higher *trans* contents are obtained with cationic Ni(II) catalysts in the presence of coordinating ligands.<sup>3</sup> Presumably, water acts as a ligand in the aqueous emulsion.

*Trans*-polybutadiene exists in two crystalline modifications, a low temperature monoclinic and a high temperature hexagonal form.<sup>6</sup> The phase transition, and the subsequent melting were observed for all polymers prepared in emulsion.



**Figure 1.** Transmission electron microscopy (TEM) image of polybutadiene particles (dispersion from entry 3 in Table 1).

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