

## UNUSUAL SYNTHESIS OF VINYL MONOMERS AND POLYMERS

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Metal catalyzed reactions enable an easier synthesis of monomers and a new approach to many polymers.

The Pd catalyzed reaction of halogeno arenes with olefins gives access to monomers in a one step reaction (Heck reaction)<sup>1)</sup>. Starting from bromo benzene derivatives and ethylene styrenes or stilbenes can be obtained. This allows to screen special reactions. As an example the anionic catalyzed reaction of 4-vinylbenzamide will be described, as the phenylogue to acrylamide<sup>2)</sup>. Derivatives of hydroquinone and terephthalic acid are obtained by the Heck reaction and give access to new LC polyesters which are soluble in organic solvents<sup>3)</sup>. The Pd catalyzed reaction of bromoarene derivatives with vinylidene fluorides results in  $\alpha$ -F-styrenes<sup>4)</sup>. The corresponding polymers are obtained by radical polymerization<sup>5)</sup>. They easily eliminate HF to form poly-(phenylacetylene)s. The ligand used in the Pd catalyzed reactions plays an important role on the product formed. Using triarylsarsine instead of triarylphosphine the major product of the reaction is the biaryl coupled product<sup>6)</sup>. The hydrogen necessary for the reduction in these reactions stems from the  $\alpha$ -hydrogen of the trialkylamine used in equivalent amounts as a base.

Pd(II) compounds are initiators of vinyl polymerization. Polynorbornene can be formed using such catalysts. These polymers show interesting properties due to the restricted change of conformation of the polymer backbone. Poly(phenylene vinylene), poly(phenylene ethynylene), and poly-p-phenylene can be prepared also by Pd catalyzed reactions<sup>7,8)</sup>. The corresponding model reactions are described using low molecular weight compounds. They give a clear indication about the possible side reactions and the limitations to molecular weight. The fact that Pd catalyzed reactions tolerate a variety of substituents allows the synthesis of a large number of new polymers

with enhanced solubility and processability. A soluble polyphenylene derivative will be described which is stable up to 600 °C. Some further examples of metal catalyzed polycondensations will be discussed.

#### References

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