

SYNTHESIS OF NOVEL DOUBLE METAL CYANIDE CATALYSTS AND POLYMERIZATION OF PO AND CO₂

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Double metal cyanides (DMC) are a versatile group of complexes that find numerous applications in catalytic conversions, e.g. as catalysts for polycondensation of diols and diacids^[1], for the ring-opening polymerization of epoxides^[2] and their co- and terpolymerization with CO₂^[3] and cyclic anhydrides.^[4] The DMC catalysts usually have a high selectivity; in case of propylene oxide ring opening polymerizations (and in contrast to e.g. alkali-based catalysts), products with low degrees of unsaturation and narrow molecular weight distributions are obtained. A major challenge in the application of DMC catalysts is that they generally feature an induction period of several minutes up to hours during which no substantial propagation is observed. The length of the induction period is affected for instance by the catalyst preparation itself but also by the presence of impurities.^[6,7] Up to this date, no reliable model exists that allows the prediction of the length of this activation step. This does not only result in decreasing overall space-time yield but also is a serious safety issue as the spontaneous initiation at the end of the induction period causes an increase in temperature due to the exothermic polymerization reactions.

Herein, we report on the synthesis of a novel type of nanoscopic DMC catalysts and the evaluation of its catalytic performance regarding the homopolymerization of propylene oxide (PO) and copolymerization of PO with CO₂. The catalysts were prepared by a two-step procedure. In the first step, a DMC-surfactant adduct is formed by co-precipitation in different solvents. Subsequently, the adduct is thermally treated to yield the active catalyst. This procedure has proven to be applicable for other heterogeneous catalysts as well.^[8] The nanoscopic catalysts show two unique features. Firstly, the prepared systems do not show an induction period, but initiate the polyreaction instantaneously upon contact with PO. Moreover, they show the highest selectivity regarding CO₂ incorporation for the CO₂/PO copolymerization, reported for DMC catalysts yet. The polymerization reactions were *online*-monitored using FTIR-spectroscopy and/or a mass flow controller, which gives crucial insights into the kinetic behavior of the catalysts. Furthermore, the development of the molecular weight distribution of the obtained products throughout the polymerization is studied (see Figure 1).

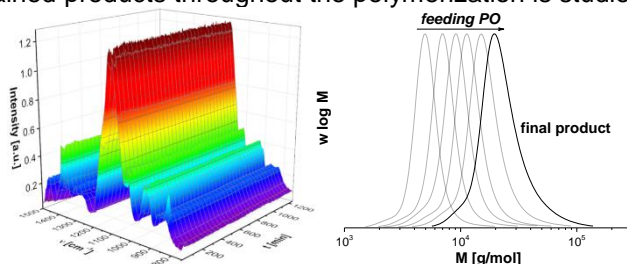


Figure 1: Left: Online-FTIR spectroscopy of the PO-homopolymerization allows to determine critical kinetic parameter. Right: Monitoring of the molecular weight distribution during the polymerization

The impact of a catalyst activation prior to the copolymerization of CO₂ and PO will be discussed. The synthesis of poly(ether)- and poly(carbonate)-polyols with narrow molecular weight distributions is presented.

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