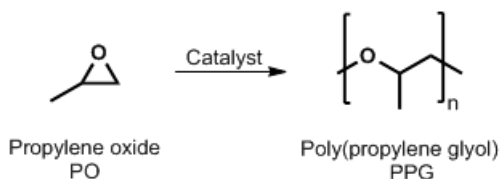# CHARACTERIZING CATALYST PERFORMANCE OF DMCS ON PO HOMOPOLYMERIZATION

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Double metal cyanide (DMC) complexes are known effective catalysts for the ring-opening polymerization of propylene oxide to generate polyether polyols (Scheme 1).[1,2] The high activity of DMC catalysts relative to basic alkaline catalysts eliminates the need for expensive removal of residual catalyst from the product. Furthermore, the poly(propylene glycol) (PPG) products prepared by DMC catalysts have - contrary to products from alkaline catalysis - a low degree of unsaturation and narrow molecular weight distributions. Latter is advantageous with respect to the resulting low viscosities. A common challenge when applying DMC catalysts is the need for an activation procedure, leading to an induction period of unknown length (Figure 1).[2,3] In a larger, usually semibatch process, PO monomer can only be added after the activation has been secured; the concentration of PO must not reach certain limits as its ring-opening is highly exothermal.
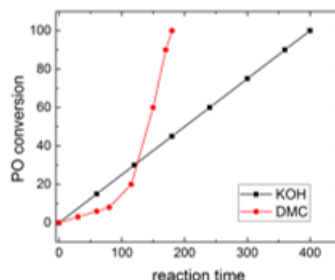

Figure 1: Dependence of induction period on type of catalyst (adapted from [4]).

Scheme 1: Homopolymerization of PO to PPG

Little is published on the intimate action of the DMC catalyst; as they are heterogeneous, studying the active sites is not so easy. Here, we report upon a study that uses PO-pulsed additions to an active system. Thermodynamic and kinetic data were obtained by monitoring the PO conversion by *online* FTIR-spectroscopy. The kinetics of the propagation step thus were studied for a variety of chain transfer agent concentrations and temperatures (Figure 2). A series of double metal cyanide catalysts with the same chemical composition could thus be characterized and compared as function of its source.

Plotting the kinetic data along Arrhenius and Eyring equation provides information on pre-exponential factor A, activation energy E_a and entropy of activation $\Delta S^{\ddagger}$, as well as enthalpy of activation $\Delta H^{\ddagger}$. This characteristic numbers are different for all catalysts studied, give deeper insights into the mechanism of the propagation step and allow to determine whether transport phenomena or the ring-opening of PO are the rate-determining reaction steps. A correlation between catalyst surface structure, especially pore size diameter, and rate-determining step will be presented. This work will also demonstrate the influence of that rate-determining step on the molecular weight distribution of resulting PPGs.
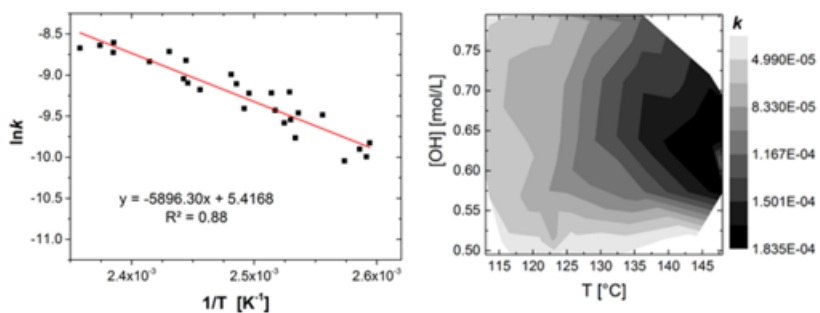

Figure 2: Left: Arrhenius-Plot to determine E_a and A from kinetic data of propagation step of PO homopolymerization. Right: Reaction rate k of propoxylation (z-axis) is plotted in dependence on [OH] and temperature.

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