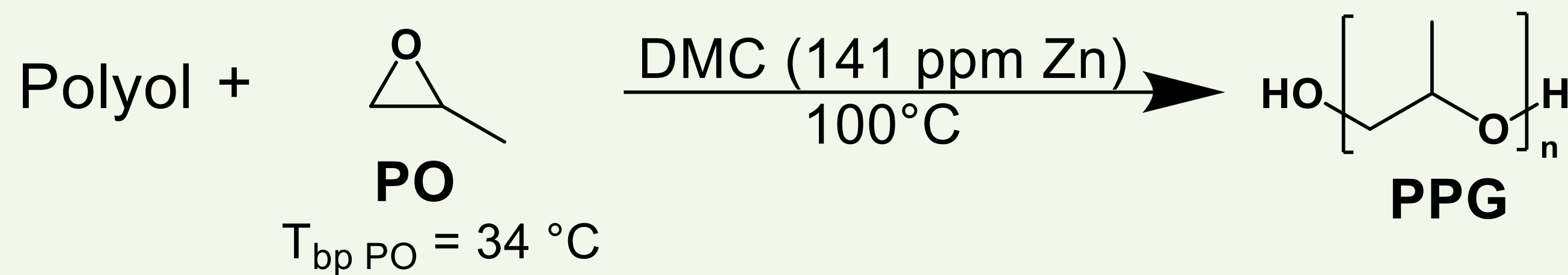
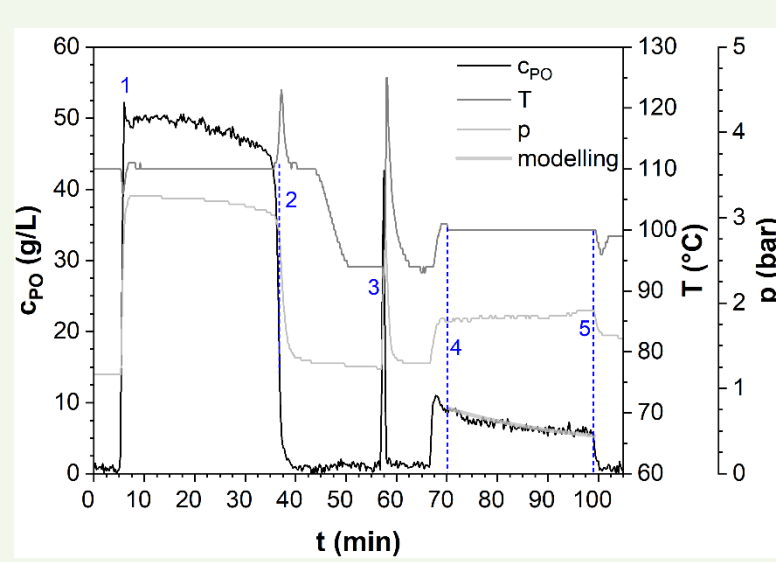


Semi-Batch operated Ring-Opening Polymerization



Experimental Method



Mass balance:

$$\dot{m}_{\text{PO}}^{\text{liquid phase}} = \dot{m}_{\text{PO}}^{\text{dosage}} + \dot{m}_{\text{PO}}^{\text{reaction}}$$

$$\frac{dC_{\text{PO}}}{dt} = \frac{\dot{m}_{\text{PO}}}{V_{\text{I}} \cdot \rho_{\text{PO}}} (C_{\text{PO}}^{\text{dos}} - C_{\text{PO}}) + v \cdot r$$

$$C_{\text{PO}}^{\text{dos}} = \frac{\dot{m}_{\text{PO}} \cdot t}{M_{\text{PO}} \cdot V_{\text{I}}} \left(H_v^c \cdot \frac{V_{\text{I}}}{V_{\text{g}}} + 1 \right)$$

- 1.) PO added;
- 2.) 1st activation;
- 3.) 2nd activation;
- 4.) Start of modelling during continuous dosage;
- 5.) End of modelling

- Assumption of pseudo-first-order kinetics:

$$r = -k_{\text{app}} \cdot C_{\text{PO}}$$

- Liquid volume balance:

$$V_{\text{I}}(t) = V_{\text{start}} + \dot{V}_{\text{PO}} \cdot t$$

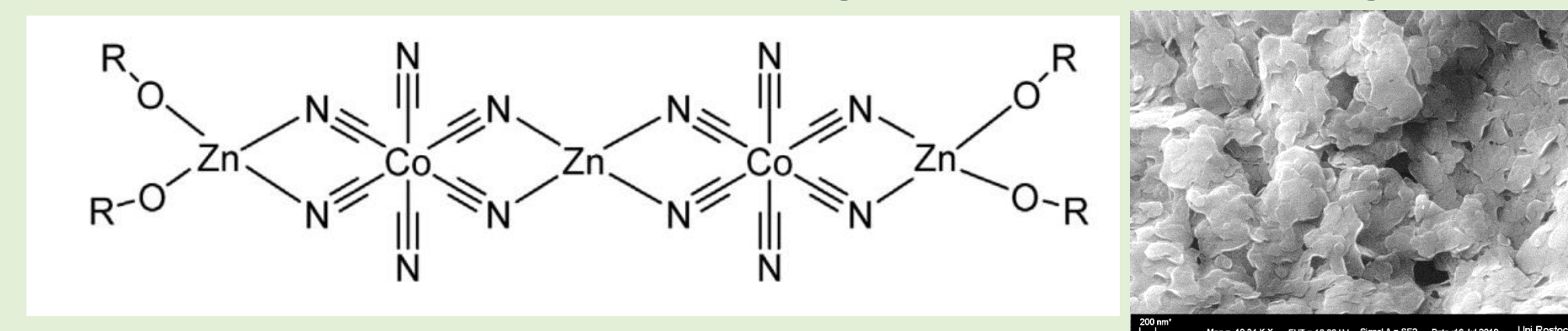
Advantages:

- Continuous PO dosage after catalyst activation (0.83 g/min).
- The influence of catalyst fragmentation on the polymerization kinetics is avoided.
- Reaction control through isothermal conditions.
- Sufficient data points collected despite the fast reaction.

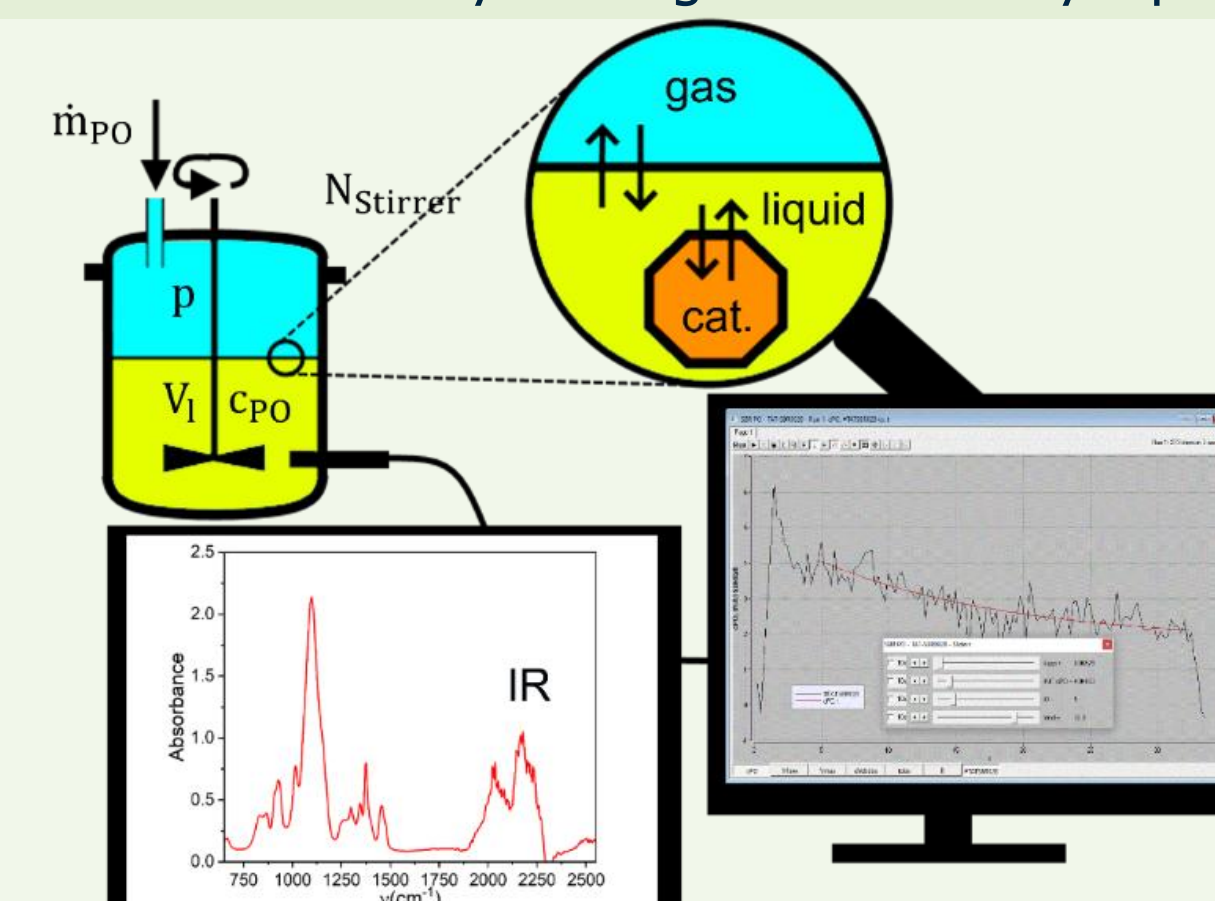
Mass Transfer Limitations:

- Exist at gas-liquid interface but has no significant effect on PDI & viscosity of resulting polymers.
- At surface-liquid interface probably dominated by ad- & desorption of reactants than by pore diffusion.

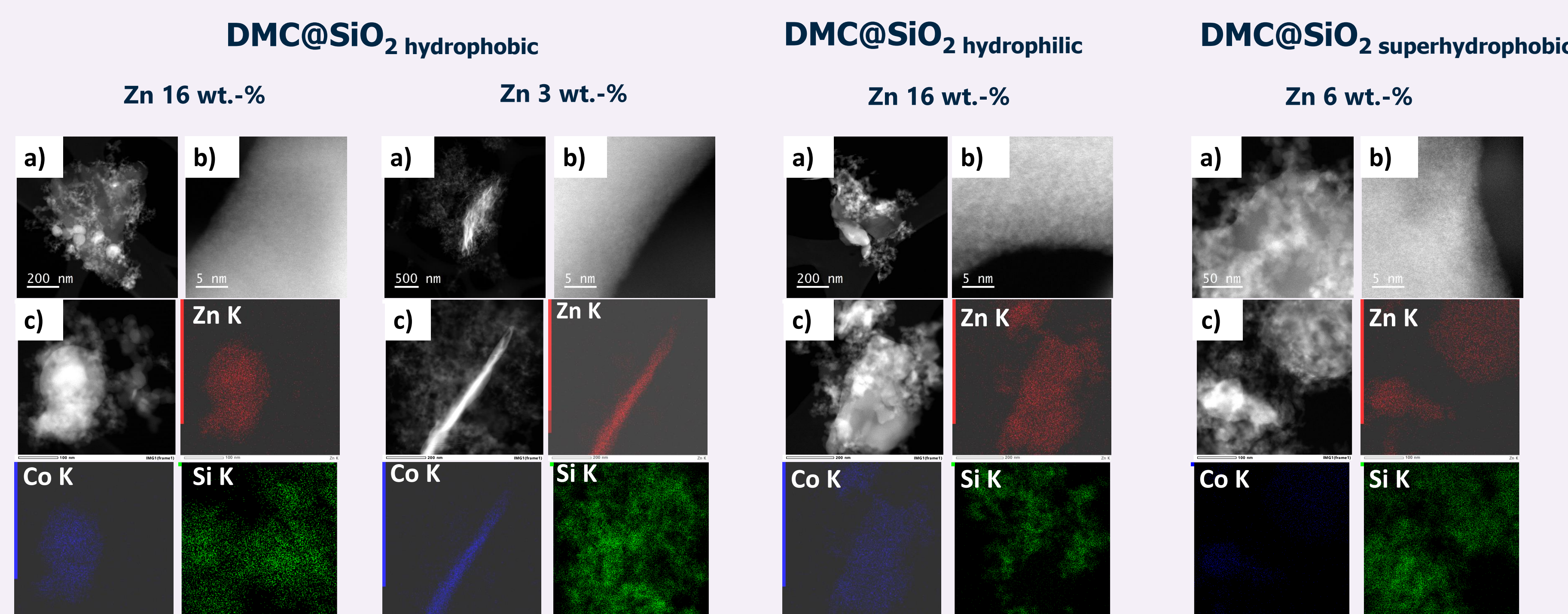
Double Metal Cyanide Catalyst



- Heterogeneous catalyst with Zn as active center.
- Synthesis through precipitation reaction of $\text{K}_3\text{Co}(\text{CN})_6$ and ZnCl_2 .
- Complexing agents like $t\text{BuOH}$ make catalyst catalytically active by introducing amorphous regions.
- Fragmentation of the catalyst during polymerization.
 - Induced by chain growth in catalyst pore.



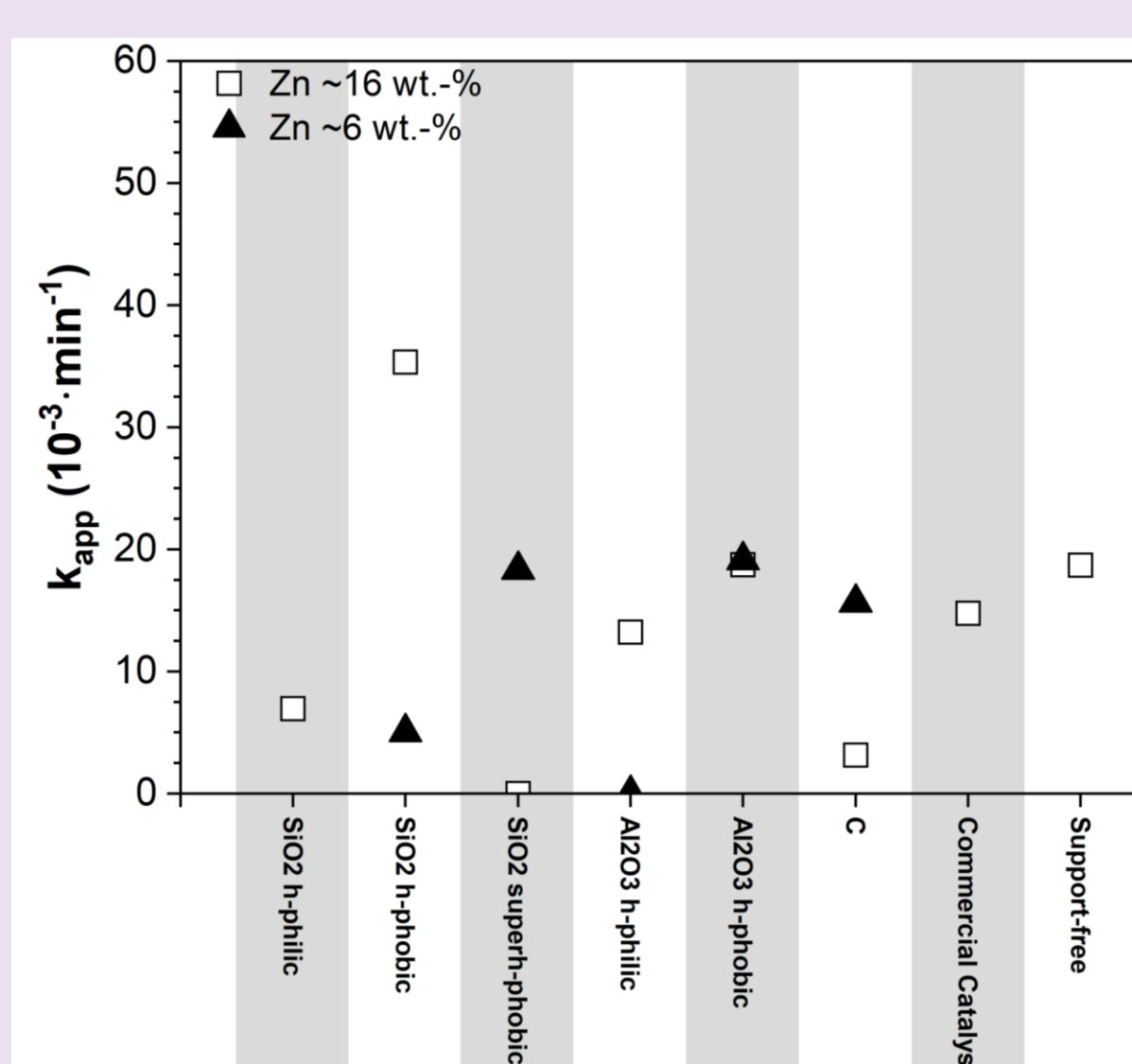
Results & Discussion



For all DMCs it was found that...

- Formation of diffuse DMC masses with dimensions of < 500 nm (determined with photocorrelation spectroscopy).
 - No crystal structure \rightarrow amorphous
- Diffuse DMC masses never occurs without support particles, but multiple support particles can stick to DMC.
- DMC particle shape and dimensions are hardly influenced by loading, catalyst support material, and surface hydrophilicity.

Polymerization Rate Constant k_{app} and Polydispersity \bar{D}



- Same initial catalyst concentration measured on Zn-concentration (141 ppm).

- Polymerization rate constant k_{app} and polydispersity \bar{D} depend on multiple factors such as loading, hydrophilicity of the surface, and support material.

- Influence of support on \bar{D} is stronger at low Zn loadings than at high loadings.

- No direct connection between k_{app} and polydispersity \bar{D} .

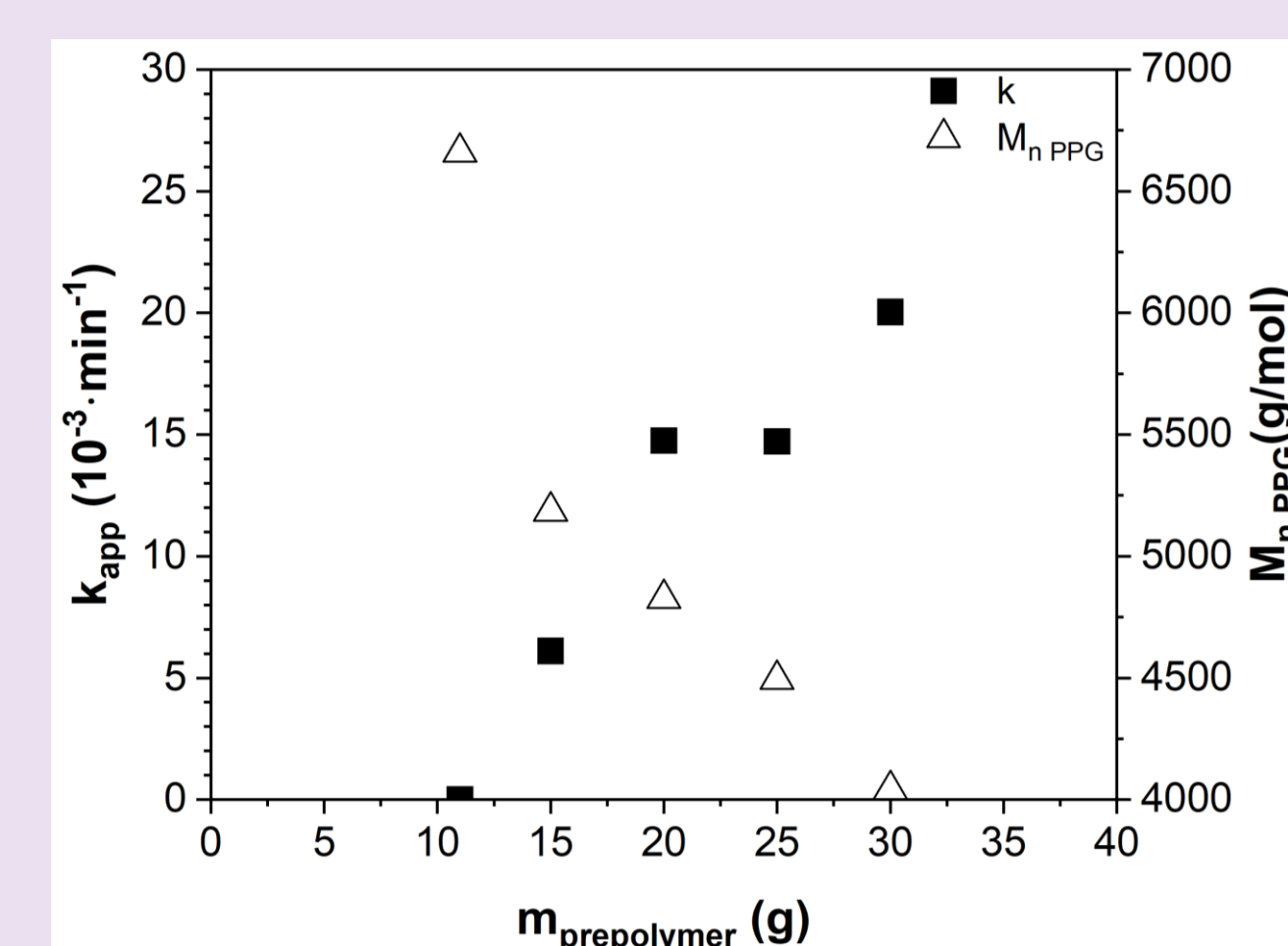
- Low loadings can lead to catalyst deactivation but also to k_{app} and/or \bar{D} comparable to the support-free and commercial catalyst.

- Chain transfer reaction rate constant $k_{\text{Chain Transfer Reaction}}$ is as well important as the propagation rate constant $k_{\text{propagation}}$.

- If ratio is still $k_{\text{Chain Transfer Reaction}} \gg k_{\text{propagation}}$ then it would be possible to obtain a polymer with narrow \bar{D} become despite low k_{app} .

- Enhancement of $k_{\text{propagation}}$ but low $k_{\text{Chain Transfer Reaction}}$ can lead to fast polymerization but broader \bar{D} .

Variation of Prepolymer Amount

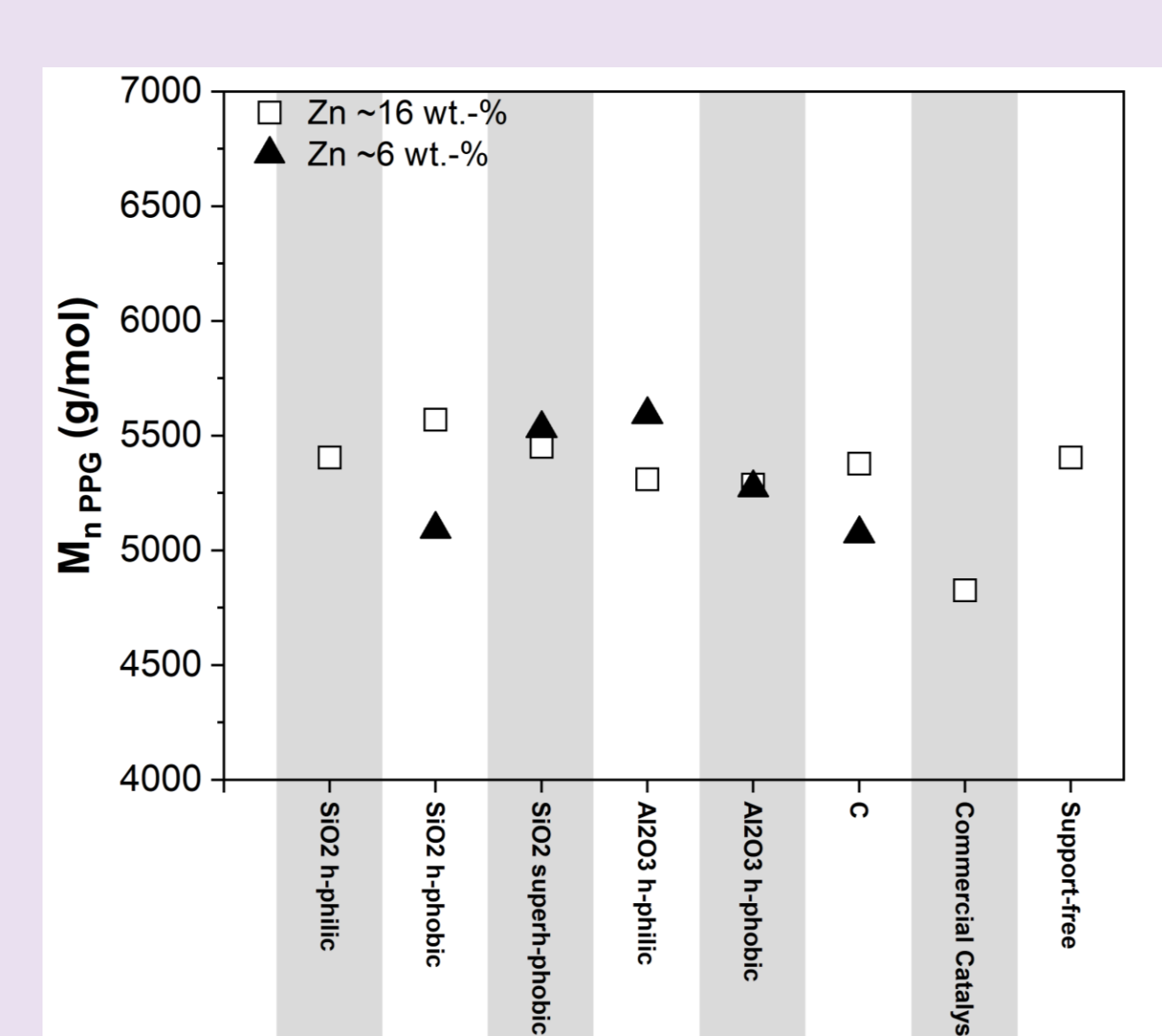


- Commercial catalyst used (Zn-concentration of 141 ppm).

- Initial polyol amount and thus the concentration of terminal hydroxy groups influence rate constant & chain length.

- Growth of existing chains is preferred over the formation of new PPG chains.

Average Molecular Weight M_n PPG



- Numeric average molecular weight M_n PPG distributed between 4600-5700 g/mol.

- Catch-up kinetics do not work the same for every supported DMC catalyst.

Conclusion and Outlook

- Supported DMC Nanoparticles are not comparable to conventional supported nanoparticles!
 - DMC nanoparticle shape and dimension not controllable via loading and support.
- Complex interplay of properties such as loading, hydrophilicity of the surface, and support material.
 - Adjustability of $k_{\text{Chain Transfer Reaction}} \gg k_{\text{propagation}}$ via support is not fully understood.
- Deposition of DMC on a support does not necessarily result in an improvement of catalyst activity nor polydispersity compared to a non-supported catalyst.