

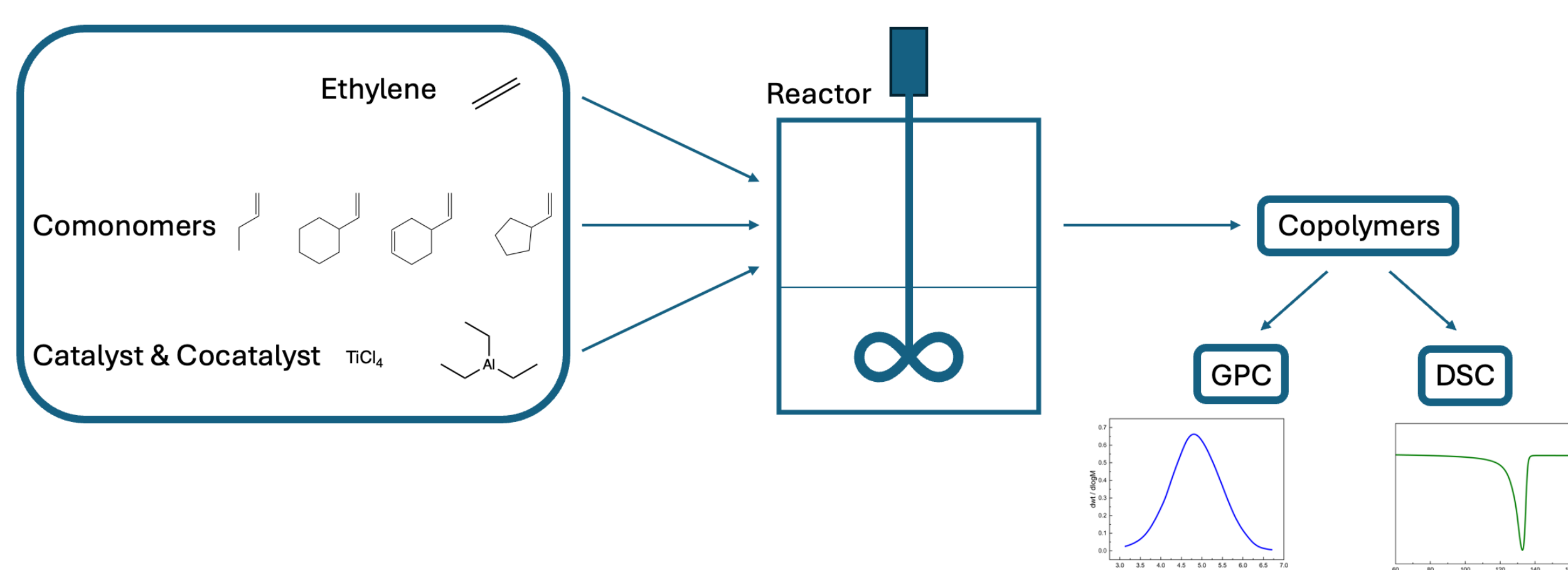
Jürgen Kranister, Christian Paulik

Institute for Chemical Technology of Organic Materials, Johannes Kepler Universität Linz, Altenberger Straße 69, 4040 Linz, Austria

Introduction:

Linear low-density polyethylene (LLDPE) is commonly produced by transition metal catalysis of ethylene and a comonomer. In this process a strictly linear polymer with well defined short chain branches (SCBs) is produced as the branches correspond to the shape of the used comonomer. Industrially mainly linear monomers including *n*-butene, *n*-hexene and *n*-octene are used.¹ Alternating the structure (e.g.: branched side chains) and amount of comonomer may lead to tailored properties.^{2,3}

Herein, the effect of cyclic SCBs on the properties of the produced polymer was investigated. Therefore, the cyclic comonomers 4-vinyl-1-cyclohexene, vinylcyclohexane and vinylcyclopentane were introduced to a standard Ziegler-Natta (ZN) catalyst polymerization process.



Scheme 1: Copolymerization of ethylene with various comonomers and subsequent analysis.

Copolymers of cyclic comonomers:

Copolymers were prepared using 10 and 35.6 mmol of cyclic monomers respectively. The reactions commenced successfully since a constant uptake of ethylene was observed over the full reaction time. Only small changes in both melting point and crystallinity were observed in DSC measurements of the obtained products as depicted in **Figure 2**. In contrast to the butene experiments the actual incorporated amount of copolymer could not be detected via GPC-IR analysis.

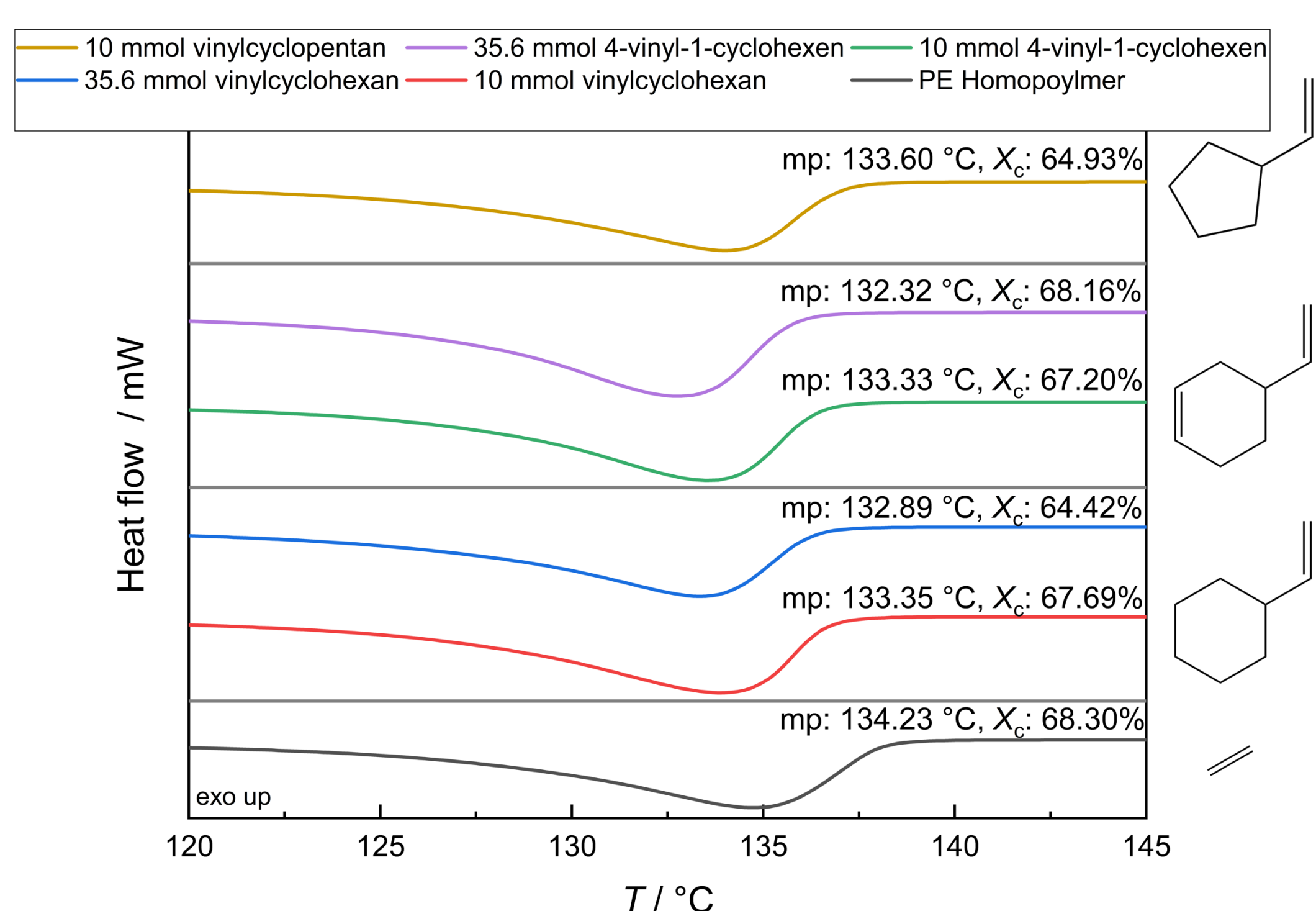


Figure 2: DSC melting curves of polyethylene copolymers prepared with different cyclic monomers.

About the author:

Jürgen Kranister is currently doing his master thesis in the field of polyolefin copolymerization.



Starting from *n*-butene:

Since *n*-butene is a commonly used comonomer in LLDPE several experiments employing different concentrations were performed.

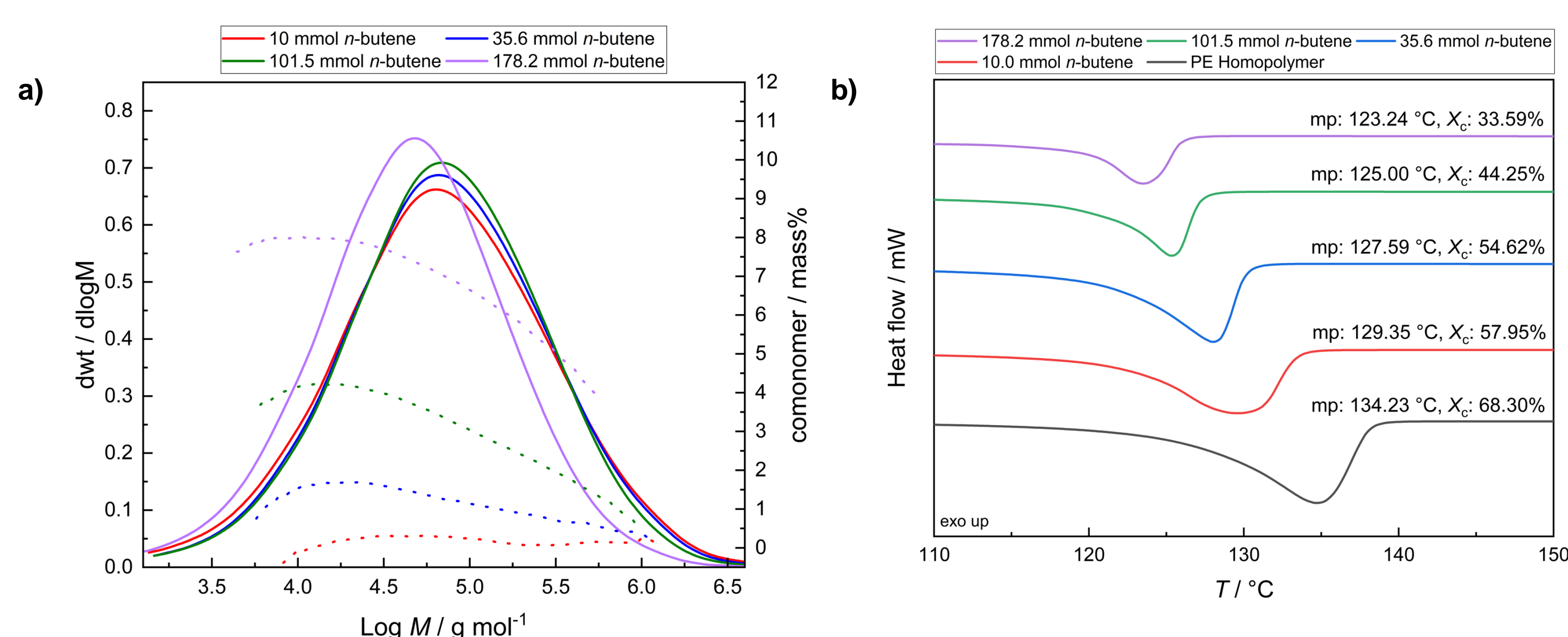
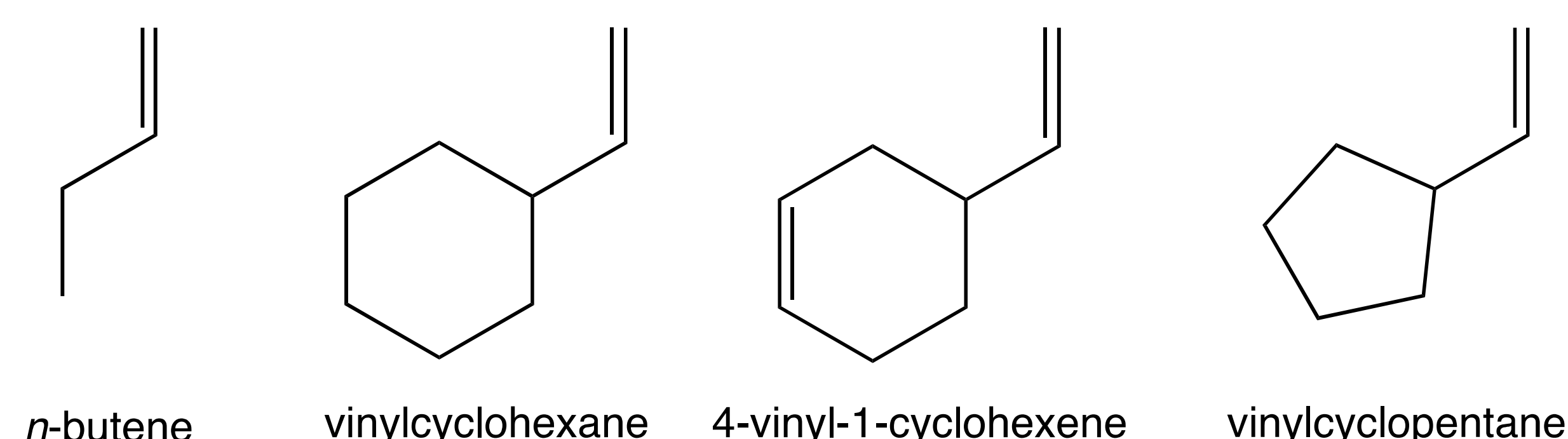


Figure 1: GPC (a) and DSC (b) analysis of the *n*-butene series. The increasing amount of butene led to lower melting points and crystallinity in the recorded melting curves.

As indicated in **Figure 1 a)**, *n*-butene could be successfully incorporated into the polymer chain. A trend of ununiform incorporation towards lower molecular weights can be seen. At the highest comonomer concentration a shift towards a lower molecular weight was observed. In **Figure 1 b)** DSC analysis revealed the relation between comonomer content and the melting point and crystallinity of the polymers.



Scheme 2: Structures of the investigated comonomers.

Scheme 2 displays the structure of the used comonomers. GPC analysis on the comonomer incorporation concentration in **Figure 1 a)** is based on the infrared response of the introduced CH₃ end-branches.⁴ These responses are absent in the cyclic capped SCBs. Therefore, this analytical method could not be applied to copolymers carrying these groups.

Conclusion:

Polyethylene copolymers were successfully synthesized via ZN catalyzed coordinative insertion polymerization.

For *n*-butene copolymers a strong influence on the melting point and crystallinity could be observe with rising comonomer concentration.

Cyclic comonomers had a limited effect on these parameters. The actual incorporated amount of material remains to be analyzed. Possible further methods include NMR-spectroscopic experiments and thermal fractioning based on the observation that comonomers tend to unevenly incorporate in the lower molecular weight segments.

References:

- Jeremic, D. Polyethylene, in: Ullmann's Encyclopedia of Industrial Chemistry, John Wiley & Sons, Inc, 2014, 1.
- Simanke, A. G.; Galland, G. B.; Baumhardt Neto, R.; Quijada, R.; Mauler, R. S. J. Appl. Polym. Sci. 1999, 74(5), 1194.
- Göpperl, L.; Cipullo, R.; Schwarzinger, C.; Paulik, C. Macromol. React. Eng. 2023, 17, 2300035.
- Blitz, J. P.; McFaddin, D.C. J. Appl. Polym. Sci. 1994, 51(1), 13.