Melting-point and crystallinity of polyethylene wax produced by different alkylaluminum co-catalysts

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Theoretical background

The polymerization of olefins using ZN catalysts is a fundamental process in the production of various plastics. These catalysts typically comprise titanium tetrachloride ($TiCl_4$) along with aluminum alkyls serving as co-catalysts. The role of these alkyls is crucial, as they are responsible for reducing the catalyst and facilitating the formation of active centers (C*) that drive the polymerization process. Factors like the type of co-catalyst, its concentration, and the specific reaction conditions all play crucial roles in determining the final properties of the PE wax.[1] In this study, the effects of different co-catalysts on PE wax were examined, with a particular focus on melting point and crystallinity.

Experimental

The experiments are carried out in a 0.5 L stainless steel multipurpose reactor with adjustable temperature and pressure. Numerous different polymerization experiments can be carried out using this setup. In this particular instance, a slurry polymerization in petroleum benzine was performed utilizing a commercial fourth-generation ZN catalyst system and a selection of co-catalysts to produce a PE wax. These included

- Triethylaluminum (TEA)
- Triisobutylaluminum (TIBA)
- Tridodecylaluminum (TDDA)
- Diethylaluminumchloride (DEAC)
- Trihexylaluminum (THA)
- Triethyldialuminumtrichloride (EASC)

To investigate the thermal properties the polymers were analysed via DSC analysis.

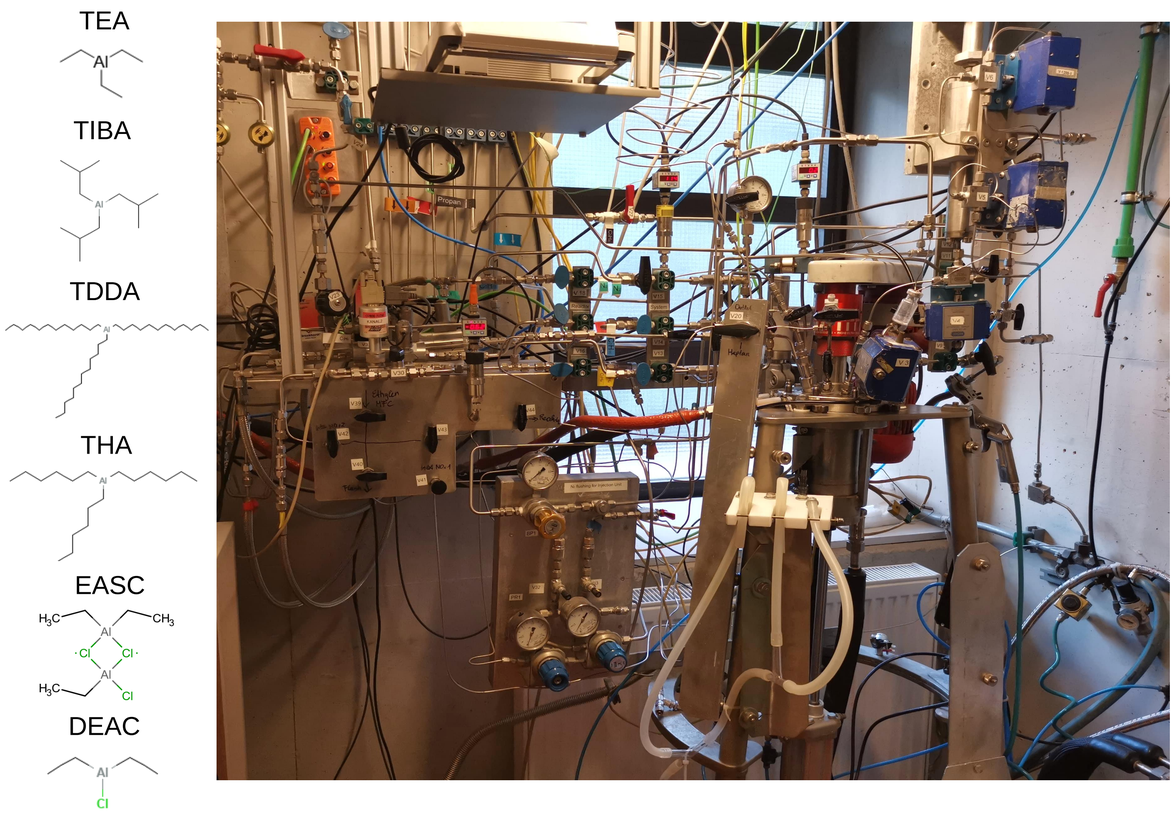

Figure 1. The co-catalysts that were used are depicted on the left site, while the experimental setup for the production of PE waxes is displayed on the right site.

Results

Each measurement yielded slightly different values for crystallinity and melting point. This lack of consistent correlation between co-catalyst choice and thermal properties as depicted in Fig 2. suggests that other factors, beyond co-catalyst selection, influence these results.[2] The observed variability in crystallinity and melting points stems from differences in the molecular weights of the PE waxes. Examining Fig 3. reveals that the crystallinity reaches a maximum at a molecular weight of approximately 12000 g mol^{-1}.

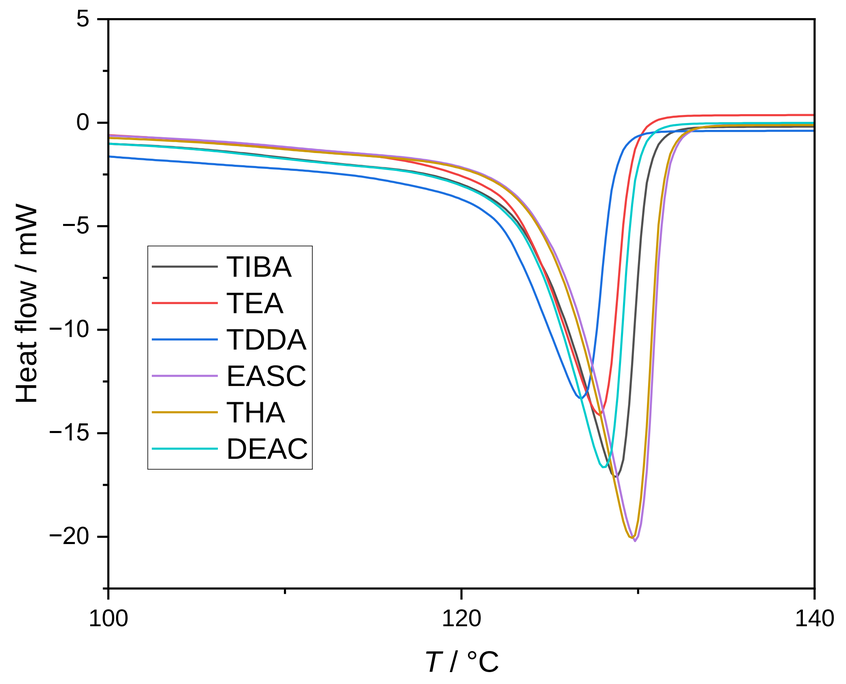

Figure 2. Melting points of PE wax samples produced with different co-catalysts.

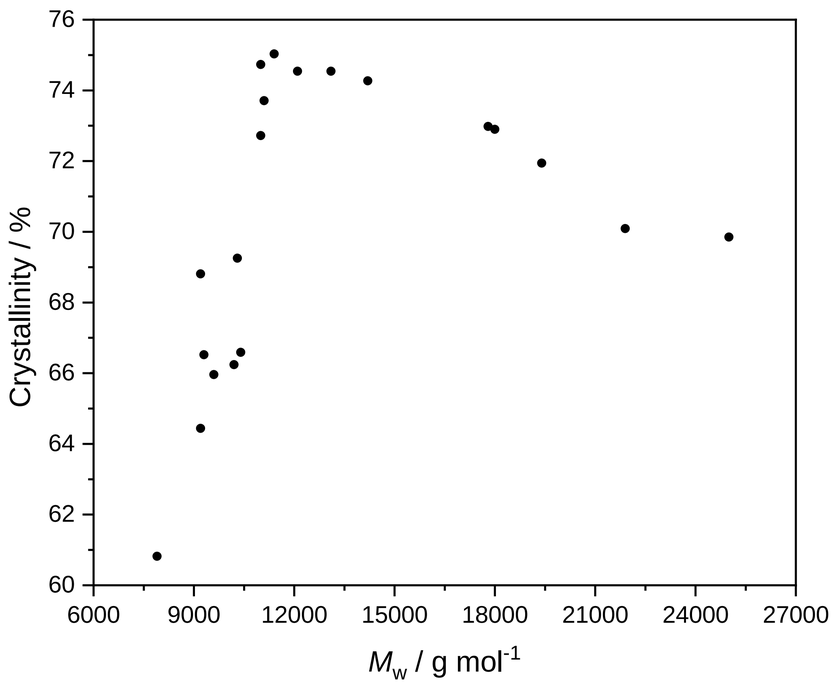

Figure 3. Crystallinity obtained from the DSC measurement is plotted against their Mw.

Conclusion

A connection between crystallinity and M_w and M_n was observed, indicating that as these molecular parameters vary, there is a corresponding impact on the crystalline structure of the polymer. Furthermore, a maximum in crystallinity for semi-industrial polyethylene could be observed. However, no apparent correlation was found between the type of co-catalyst used and the thermal properties of the resulting polymer. This suggests that the choice of co-catalyst does not directly affect the crystalline properties.

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Currently working as an PhD student in the field of polyolefines.

References

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2. Krumme, A.; Lehtinen, A.; Viikna, A. Eur. Polym. J. **2004**, 40, 371–378.