Supported Hybrid Early and Late Transition Metal Catalysts for the Synthesis of Polyethylene with Tailored Molecular Weight and Chemical Composition Distribution

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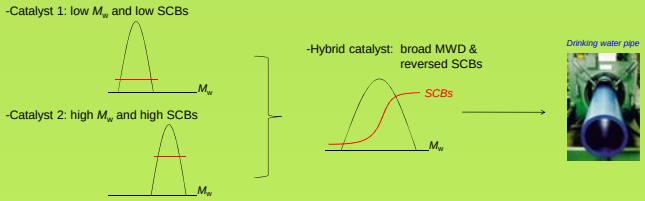
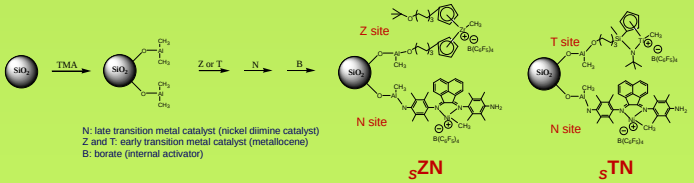
Hybrid Catalyst for Bimodal Polyolefin in a Single Reactor

- Hybridization of two single-site catalysts with different properties could control MWD & SCBs of polyolefins
- Resultant polyolefin has superior crack resistance and high stiffness, and it is promising for producing high performance pipes

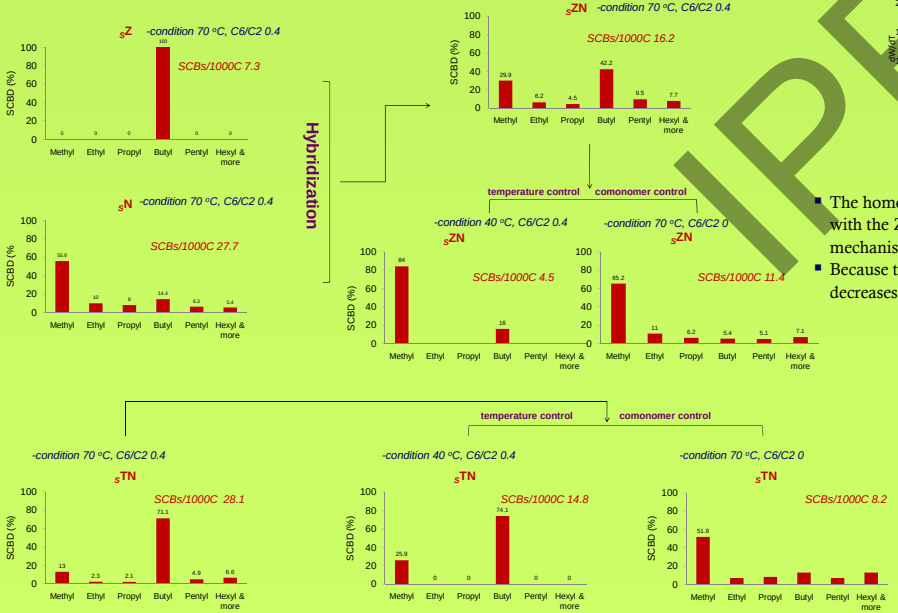


Synthesis of Supported Hybrid Catalysts



N: late transition metal catalyst (nickel diimine catalyst)
Z and T: early transition metal catalyst (metallocene)
B: borate (internal activator)

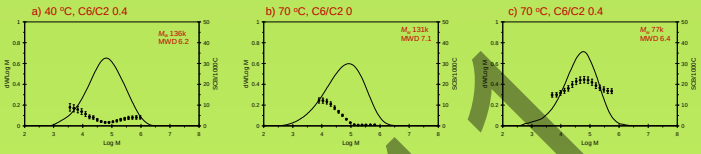
Tailored Short Chain Branch Distribution with Hybrid Supported Catalysts (by ^{13}C-NMR)



- N controls various SCBs by temperature, and Z controls particular SCBs by comonomer feed.
- T incorporates more SCBs than Z.

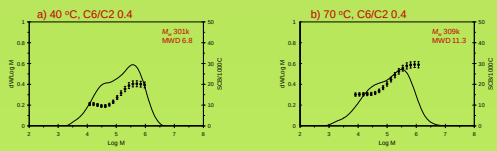
MWD and SCB Frequency of Polyethylene Made with $_S$ZN and $_S$TN (by GPC-IR)

$_S$ZN



- The low M_w population is made with the N catalyst, and the high M_w population is made with the Z catalysts.
- The SCB frequency of the lower M_w polymer increases when the temperature changes from 40 °C to 70 °C because of *chain walking* frequency for the N catalyst increase at higher temperature.
- No SCBs are detected in the higher M_w population in absence of 1-hexene, since SCBs are formed by 1-hexene incorporating by the Z catalyst.

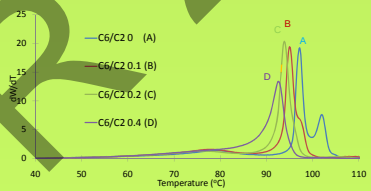
$_S$TN



- The polymers with bimodal MWD and reverse comonomer incorporation are made.
- High amount of SCBs are incorporated in the higher molecular weight region of the distribution, resulting in polymer with reverse SCBD.
- At higher polymerization temperature (70 °C), the polymer becomes even more branched.

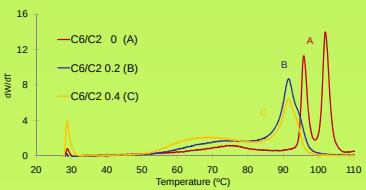
Chemical Composition Distribution (CCD) of Polyethylene Made with $_S$ZN and $_S$TN (by CEF)

$_S$ZN



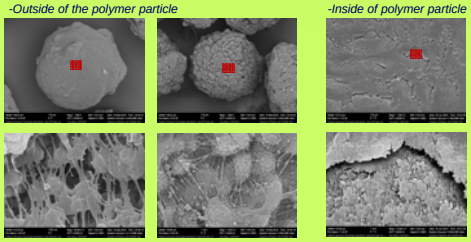
- The homopolymer A had trimodal CCD; the high-crystallization peak (102.1°C) is made with the Z catalyst, and other two peak containing SCBs made via the *chain walking* mechanism was made by N catalyst.
- Because the Z active sites incorporate α-olefin than the N sites, temperature with Z decreases much more significantly as the higher 1-hexene amounts.

$_S$TN



- The CCD for homopolymer A is similar to that for $_S$ZN.
- The polymer with the highest elution peak is made on the T sites.
- The other two peaks at lower temperature are made with the N sites.

Morphology of Polyethylene Made with Hybrid Catalysts (by SEM)



Conclusion

1. GPC-IR and CEF results show that supported two types of catalysts behaved independently of each other.
2. The polymers with distribution SCB lengths were produced without α-olefin by the nickel diimine catalyst via the chain walking mechanism, while the metallocene component needs α-olefin to produce branched chain.
3. The combination of the Z, T and Z catalysts having unique characteristics led to polymers having broad and bimodal MWD and trimodal CCD.
4. Depending on the polymerization conditions, an inverse distribution of SCBs across the MWD could be obtained, where the SCB frequency increases with increasing molecular weight.
5. The formation of free-fouling polymer particles confirms that the catalyst sites were strongly supported onto SiO_2.