

Current and future developments in alkene polymerization

- ❖ Synthesis of polyolefins with long chain branches;
- ❖ Synthesis of block copolymers via **chain-shuttle polymerization**;
- ❖ Nanocomposites based on polyolefins via *in-situ* polymerization;
- ❖ **Ethylene/polar alkenes copolymerization.**

Block copolymers via chain-shuttle polymerization

The new **polyolefin block copolymer called INFUSE**

Dow Company

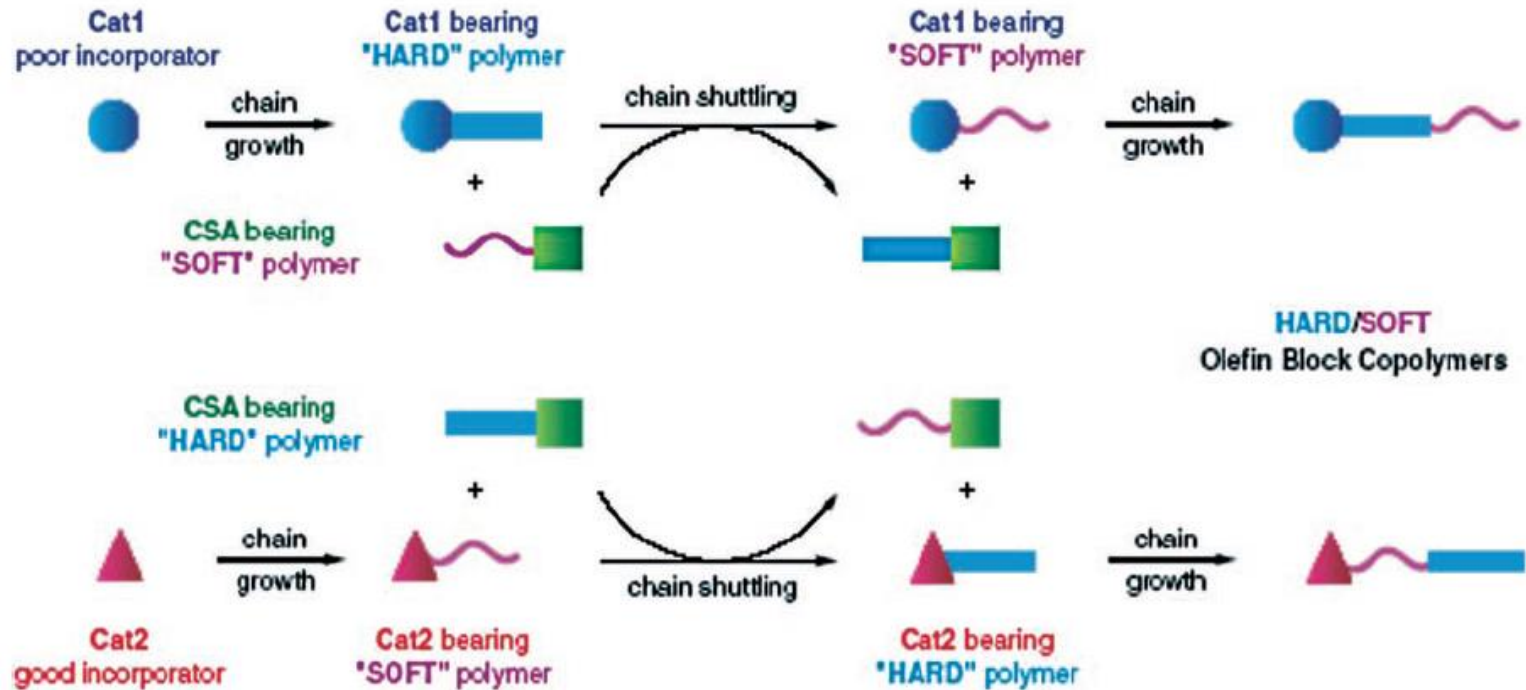
The principle:

Application at the same time, in the presence of a chain-shuttling agent, of two different catalysts, that when separately used would lead to structurally different polymers.

*The name of **chain-shuttling** defines the **REVERSIBLE** movement of the growing polymer chain between two different catalytic sites, in such a way that portions of the same polymer chain are synthesized by the two different catalysts.*

The two catalysts are featured by a **different selectivity**, that can be either a different **stereoselectivity** (stereoblocks polymers are obtained) or a different **chemoselectivity towards two monomers** (polymer with **blocks differing in the composition** are obtained).

Chain-shuttle polymerization



The synthesis of copolymers with blocks differing in the composition via chain-shuttling is realized by using a mixture of two monomers and choosing two catalysts that have a different chemoselectivity towards the two monomers.

The target was to obtain a block copolymer featured by alternating blocks of crystalline and amorphous polymers: obtaining a hard and soft copolymer.

The two monomers used are ethylene and 1-octene: the PE with a low content of 1-octene is a semicrystalline polymer (hard) with $T_m = 135\text{ }^\circ\text{C}$; the PE with a high content of 1-octene is an amorphous polymer (soft) with $T_g < -40\text{ }^\circ\text{C}$.

A three component system is applied. Features of the three components:

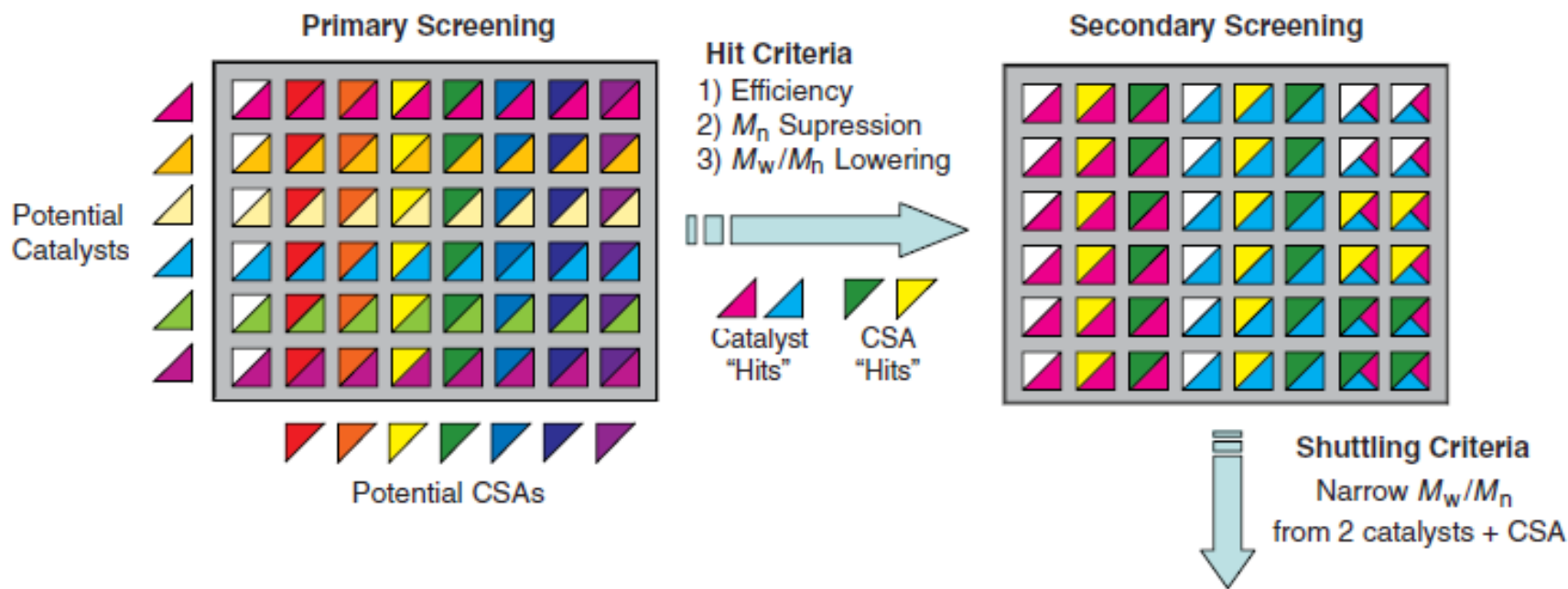
- ❖ Being active under the same reaction conditions;
- ❖ Do not be the poison of one each other;
- ❖ The chain-shuttling agent must act in this way towards both catalysts;
- ❖ The chain-shuttling process must be **REVERSIBLE**.

The catalytic system is very *versatile*

- ❖ the hard/soft ratio in the polymer is controlled by the relative amount of the two catalysts;
- ❖ the content of the two monomers in the relevant blocks is controlled either by the content of the two monomers in the starting mixture or by varying the catalyst;
- ❖ the average length of the blocks is controlled by the $[CSA]/[monomer]$ ratio.

The discovery of the catalyst:

Combinatorial catalysis and high-throughput screening



Post-metallocene catalysts

