High-Performance Polyolefins

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Novel Olefin Block Copolymers through Chain-Shuttling Polymerization

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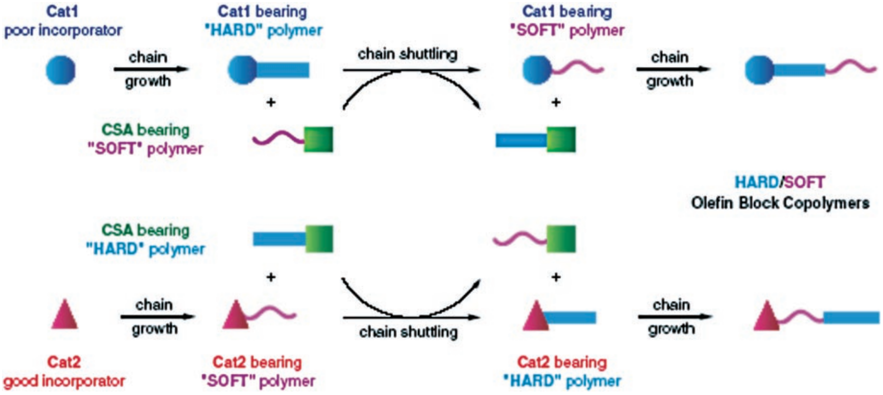
Polyolefins, particularly polyethylene (PE) and polypropylene (PP), are *the* commodity polymers in the field of technical plastics with an amazingly broad range of applications. Since their first production through Ziegler–Natta systems,[1] the use of defined molecular catalysts, such as metallocene dichlorides, have led to a renaissance of this also economically important field and to a revolutionary advancement of the material properties in general. Both regiospecificity and stereoselectivity[3] as well as the architecture (number and length) of branches[4] can be controlled at will by these tailor-made catalysts. In addition to homopolyolefins, copolymers also broaden the characteristic scope of polyolefins, particularly by incorporating higher α-olefins (e.g. ethylene-co-1-octene).[5] Thus, from these simple olefin monomers, materials ranging from the conventional hard and highly crystalline thermoplasts to flexible elastomers are accessible.

Is the field of polyolefins thereby fully established, or is there room for new approaches and products? How can novel properties be generated, and where do new developments take us? The keyword here is "high-performance polymers" with a precisely adjusted architecture. Behind it lies the idea of "designing" polyolefins such that they may enter new material sectors through a special functional pattern. Besides a controllable microstructure (regiospecificity and stereoselectivity), this idea can be realized in particular through the synthesis of block copolymers.

The synthesis of diverse block copolymers through living polymerizations is an important method applied by many production facilities and research establishments worldwide.[6] In this context, the type and length of the blocks can be regulated by sequential addition of monomers. However, these mostly anionic and radical polymerization reactions result in polyolefins without microstructural control. To the contrary, if coordinative, living polymerization reactions are applied, the polymer structure can be influenced by the ligand design and through suitable choice of the metal component. Unfortunately, those catalysts that allow control of the microstructure are mostly unable to generate block structures with chemically different monomers. In particular, the economical aspect of this method is unfavorable: each catalyst molecule produces only one polymer chain. This inefficiency drives up the costs of large-volume production.

A new catalytic synthesis strategy, namely "chain-shuttling" polymerization,[7] has led to promising results. In this approach, two different catalysts that generate different polymer structures are used. By transferring polymer chains from one catalyst to the other, block copolymers that consist of segments with different microstructures can be prepared (e.g. semicrystalline (hard)/amorphous (soft); Scheme 1). Thus, block copolymers that combine different mechanical properties in one polymer chain can be produced.

To apply chain-shuttling polymerization, a chain-transfer reagent that enables reversible transfer of the polymer chain is necessary. A transfer of the polymer chain onto metal alkyls (alkyl–polymer exchange) is known and has been most intensively examined for (but is not restricted to) aluminum alkyls (e.g. methylaluminoxane (MAO), trimethylaluminum).[8] For example, magnesium, zinc, and beryllium alkyls have



Scheme 1. Principle of "chain-shuttling" polymerization (CSA: chain-shuttling agent). Reprinted from Reference [13] with permission from the AAAS.

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likewise proven themselves to be active chain-transfer reagents. Moreover, there have been reports on irreversible as well as reversible procedures of chain transfer.[9] Furthermore, diethylzinc has recently been described as being particularly efficient as a chain-transfer reagent (in catalyzed chain growth).[10]

If one would now select catalysts that are able to take part in a chain-transfer reaction, only one suitable, reversible chain-reaction reagent would be needed to ensure the polymer chain transfer between the catalysts. If a reverse transfer to the same catalyst takes place, then the respective block section is prolonged. During a transition of catalyst 1 to 2 (and vice versa), a second polymer section is inserted adjacent to the first one. To obtain block copolymers, the transfer rates of the polymer chains must be slightly below the rate of polymerization. This chain-shuttling methodology generates enormous variability. The length and number of the inserted blocks can be designed on a large scale through the selection and quantity of chain-transfer reagents. The variation and relative proportion of the two catalysts, as well as the addition and ratio of monomers, allow fine-tuning of the respective segments (microstructure, co-monomer contents, etc.).

Chien and co-workers[11] and Brintzinger and Lieber[12] independently reported on the synthesis of stereoblock-PP through a reversible chain transfer between two catalyst species with different stereoselectivities. However, the results showed that mixtures of atactic and isotactic polymer predominantly formed and only a small percentage of stereoblock copolymers occurred. Furthermore, Fink and Pryzbyla investigated an elegant strategy for generating isotactic/syndiotactic PP-block structures through mixing correspondingly selective metallocenes on carrier surfaces.[13]

The new continuous-feed[14] chain-shuttling polymerization approach of Arriola et al.[15] is characterized by suitable choice of catalysts and the chain-transfer reagent to develop quantitatively uniform block copolymers. The goal was to generate polymers made of sections of amorphous (soft) and semicrystalline (hard) polyolefins, and merge the high melting points of the hard block structures ($T_m \approx 135\,°C$) with the low glass-transition points of the soft structures ($T_g < -40\,°C$). A polymer with these melting characteristics provides a material that remains elastic even at elevated temperatures.

The principle of this synthesis is simple. A catalyst (1) is used which generates hard, semicrystalline polyolefins from a mixture of ethene/higher α-olefin (in this case, 1-octene), as a result of a high insertion rate of ethylene and a low one for 1-octene. Additionally, a second catalyst (2) is chosen which displays an increased selectivity for 1-octene and generates an amorphous, soft polymer from the same mixture, as the long side chain of the higher α-olefin prevents crystallization of the polymer chains.

With the help of the high-throughput procedure, Arriola et al. investigated a series of catalysts and chain-transfer reagents to find suitable candidates that are also active under the required polymerization conditions ($T = 120\,°C$).[16] For the reversible chain transfer, diethylzinc was proven effective. Zirconium bis(phenoxyimine)[17] (catalyst 1) and hafnium pyridylamide[18] (catalyst 2) were chosen.

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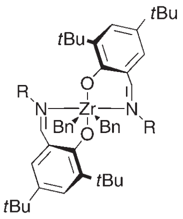
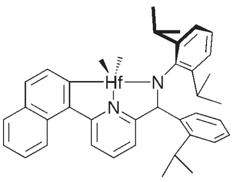


R: 2-methylcyclohexyl

2



When the mixture of catalysts 1 and 2 were applied to the polymerization of ethylene/1-octene, the result was a cloudy polymer blend of hard and soft polyolefins. Analysis using gel permeation chromatography (GPC) revealed a bimodal distribution of molecular weights. In the presence of the chain-transfer reagent diethylzinc, the reaction generated a transparent polymer with a monomodal molecular-weight distribution and a low polydispersity (Figure 1).

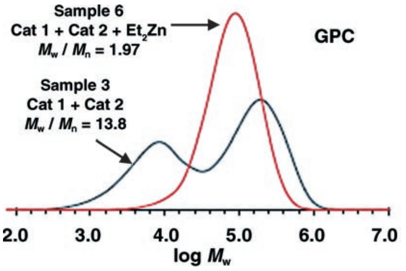


Figure 1. Molecular-weight distribution of the polymer mixture (black) and the homogeneous block copolymer obtained through chain-shuttling polymerization (red). Reprinted from Reference [13] with permission from the AAAS.

The fact that a homogeneous polymer with a narrow molecular-weight distribution can be generated by polymerization with two catalysts of different monomer selectivity and molecular weight indicates a fast chain-transfer reaction. The fractionation of both polymer samples described above showed that in the former sample, semicrystalline as well as amorphous polymer were formed. However, in the second sample, solely block copolymers were produced. The generated novel block copolymers have molecular weights that are only slightly below the mean value of the polymer blend. The molecular weight distribution is narrow (polydispersity index ≈ 2). Such well-defined polymers are usually only found when uniform, individual catalyst species are used. This observation further indicates the multiblock nature of the copolymers; such a homogeneous molecular-weight distribution can be regulated only by multiple chain transfer. The melting point of the block copolymer is only a few degrees lower than that of the semicrystalline homopolymers. The copolymers exhibit excellent elastic properties at much higher temperatures than the conventional statistical copolymers of the same densities. Thus, thermoplastic elastomers from simple olefin monomers are available for applications at higher temperatures.

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