Core–Shell Particles

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Spatially Resolved Catalysis for Controlling the Morphology of Polymer Particles**

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Morphology control is essential when optimizing the properties of polymer blends and inorganic–organic hybrid materials.[1,2] Properties such as mechanical stability, impact strength, or scratch resistance are adjusted by the homogeneous incorporation of a second polymer or inorganic particles into the blend. However, simple blending of two distinct materials can lead to ill-defined mixtures with an irregular component distribution. Block, graft, or other copolymers can be used as compatibilizers to overcome these drawbacks.[3,4] Synthesis of these polymers, however, requires living polymerization techniques, and prediction of the resulting morphologies by employing theoretical models is difficult. In another approach, which is mainly used for dispersions that are applied as paints and coatings, core–shell particles that consist of two polymers are generated by emulsion polymerization.[5] Both processes are unsuitable for olefins and the sensitivity of the required catalysts means that aqueous emulsions are not applicable to olefin polymerization. Compatibilization of polyolefins with different polymers is also a challenge because of the lack of compatibilizing block copolymers.[6–7] The problem of obtaining polyolefins with a core–shell morphology can be only partially solved by using a complex reaction sequence,[8] in which the polyolefin obtained after a first gas-phase polymerization is transferred into another reactor that contains the second monomer.[9] However, this process is both expensive and complicated, and needs to be adjusted for special polymer mixtures. The development of versatile methods for the generation of more complex polymer morphologies in particles, especially for polyolefins, remains a challenge.

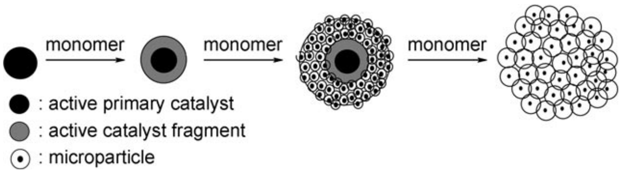

Figure 1. Fragmentation process of a pure silica catalyst (the pure "core" of a core–shell catalyst).

It is already known that supporting catalysts are required to adjust the morphology (such as size and bulk density) of polyolefin particles.[8] The control is mainly achieved by shape replication of the supporting particles in the product particle. The ability of a support to fragment into smaller particles during the polymerization process (Figure 1) is decisive for the replication process, which generally occurs in a stepwise fashion from the outer to the inner shell of the support (Figure 1).[10]

We proposed the use of a replication effect to not only control the shape of the particles, but also to generate an inner morphology (core–shell structure) during polymerization. We thus anticipated that the loading of different catalysts in different layers of a spherical support would result in the spatially resolved formation of different polymer layers in a product particle. A nanostructured catalyst system can act as a template for the formation of the final morphology in the product particle (Figure 2). As both the immobilized catalysts and the polymers were expected to be migrationally stable under the reaction conditions, the final product should represent the structure of the initial catalytic system.

To verify this concept, we studied the formation of a core–shell product particle that consists of different types of polypropylene (PP). We report herein a catalyst system in which two metallocene catalysts produce polypropylene with different tacticities. The two catalysts are spatially resolved in the different layers of an inorganic–organic hybrid particle with an inorganic core and an organic shell.

The production of the well-defined core–shell catalyst particles is based on three synthetic steps: 1) formation of a

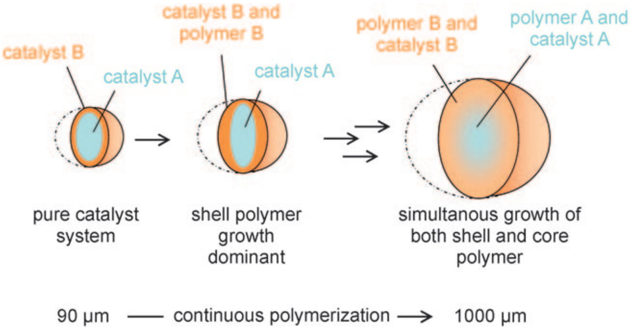

Figure 2. Olefin polymerization induced by a particle with two catalytic domains. Formation of two distinct polymers in one step under constant reaction conditions.

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solid inorganic core that contains the metallocene catalyst A, 2) coating the core with an organic shell of latex particles (prepared according to Ref. [11]), and 3) immobilization of the second metallocene catalyst B on the organic shell. Since the presence of a co-catalyst (methyl aluminoxane), which also acts as an adhesive agent for the shell and for the metallocene, is required, steps 2 and 3 are carried out simultaneously (Figure 3). Bis(methylcyclopentadienyl) zirconium dichloride (MCP), which forms atactic PP, was chosen as catalyst A, immobilized in the center of the particle. *rac*-(Dimethylsilyl-bis(2-methylbenzindenyl) zirconium dichloride (MBI) was selected as catalyst B, as it generates an isotactic PP (see Figure 7).

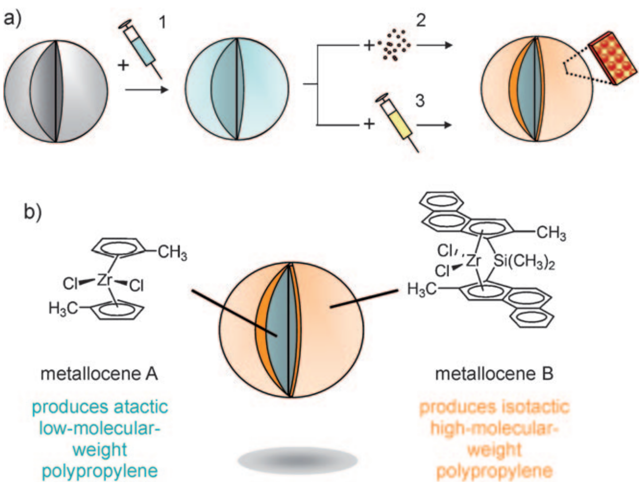

Figure 3. a) Synthesis of a core–shell catalyst. 1) Impregnation of a core catalyst with metallocene A. 2) Addition of polystyrene nanoparticles as support for the shell catalyst. 3) Addition of a solution of metallocene B for incorporation of the latter into the shell. b) One of the spatially resolved core–shell particles used for propene polymerizations.

Formation of the hybrid support with a homogeneous shell of latex particles was proved by a series of microscopic techniques. The final particle size, before olefin polymerization, was determined by scanning electron microscopy (SEM) to be in the range 50–100 μm. As the latex particles were tagged with a fluorescent perylene dye,[12] laser scanning confocal fluorescence microscopy (LSCFM) was used to selectively visualize formation of the shell (Figure 4, center). The image revealed a fluorescent halo formed by a shell of latex particles several micrometers thick, which was adsorbed on the outer surface of the silica but not in the pores. Additionally, SEM showed the formation of two distinct morphologies that corresponded to an inorganic core with an organic shell (Figure 4).

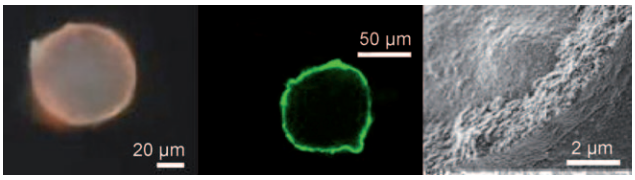

Figure 4. Core–shell formation of an inorganic–organic hybrid particle. Optical microscopy (left), LSCFM (center), and SEM (right) pictures of a core–shell catalyst particle.

Once the formation procedure for the core–shell systems was established, studies with selective loading of either core or shell were carried out to prove exclusive loading in the respective domains. Gas-phase polymerizations of propene were carried out using the supported hybrid particles. According to SEM experiments, spherical polyolefin particles were obtained in all cases (Figure 5). The resulting size depended on the polymerization time, which varied from 70 to 140 μm (see the Supporting Information for time-elapsed video microscopy pictures).

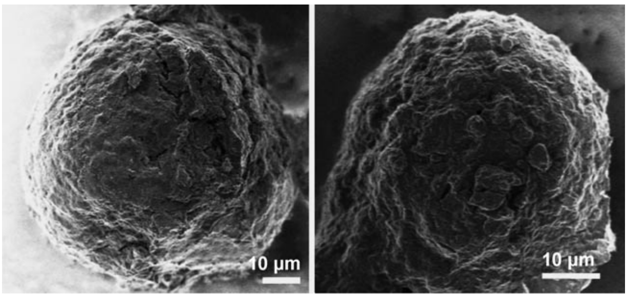

Figure 5. Typical SEM images of two PP core–shell particles obtained after 1 h under identical polymerization conditions (50 °C, 4 bar); catalyst: MBI shell, MCP core.

SEM images of the particles showed that either the olefin was polymerized in the core by catalyst A or in the shell by catalyst B (Figure 6). In the first case, an atactic polypropylene of low molecular weight ($M_w = 3.5 \times 10^3\,\text{g}\,\text{mol}^{-1}$) was obtained from the MCP supported in the core. In the second experiment, the MBI immobilized in the shell, produced high-molecular-weight isotactic polypropylene ($M_w = 2.1 \times 10^4\,\text{g}\,\text{mol}^{-1}$).

Supports that contained both catalysts with the spatial arrangement depicted in Figure 3b were investigated (Figure 5). The loading of the two active single-site catalysts in the core and the shell of the particle was confirmed by the bimodal GPC data ($M_w = 1.7 \times 10^4$ for isotactic PP, and $3.2 \times 10^3\,\text{g}\,\text{mol}^{-1}$ for atactic PP). These values correspond to the results obtained in the experiments that used MCP and MBI

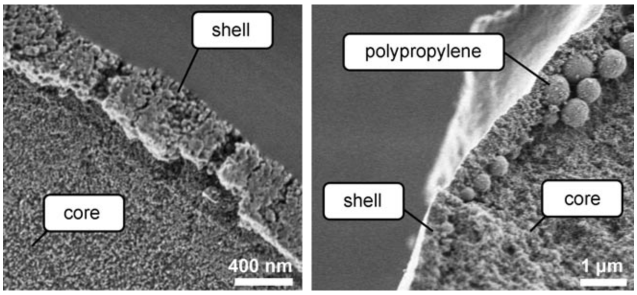

Figure 6. SEM pictures of particles exclusively loaded with catalyst B in the shell before (left) and after polymerization (right).

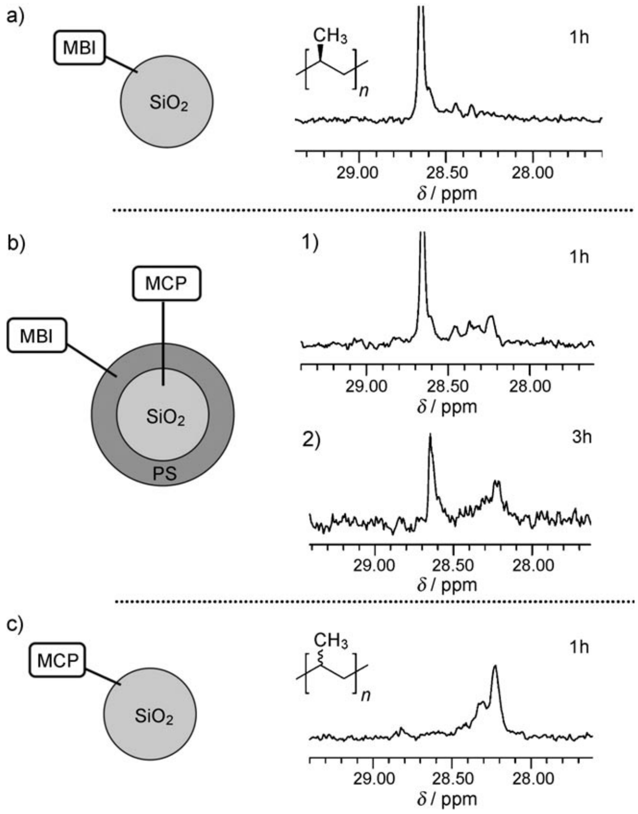

Figure 7. ^{13}C NMR spectra of a) polypropylene (methine region) produced by MBI in the core, b) samples from the polymerization reaction with the core–shell particles: 1) a predominantly isotactic polymer is formed after 1 h of polymerization and 2) a mixture of atactic and isotactic PP is formed after 3 h of polymerization, and c) polypropylene produced by MCP in the core.

separately, and showed that both catalysts in the mixed system were active and did not affect each other; however, the formation of molecular blends was not excluded. Although the polymerization process and final products were monitored by video microscopy, LSCFM, differential scanning calorimetry (DSC), and gel permeation chromatography (GPC), quantitative ^{13}C NMR spectroscopy provided the best insight into the polymerization process as two very distinct primary structures were formed. Different polymer samples were taken at different reaction times and the tacticity determined by ^{13}C NMR spectroscopy (Figure 7). PP obtained from MBI or MCP supported on silica was used as reference. Only isotactic polypropylene was produced at the early stage of the polymerization, thus proving that only metallocene B, which was located on the surface of the core–shell particles, was accessible to the monomer at this stage. On the other hand, samples taken after longer reaction times (3 hours) contained an increasing amount of the atactic low-molecular-weight polypropylene. It can be assumed that the shell of the latex particles starts to fragment as the reaction proceeds, while the monomer can also diffuse into the silica core that contains metallocene A. The formation of different types of PP during the course of the reaction proves that spatially resolved metallocenes are loaded on the support.

The observed behavior confirms that the model of the established layer-by-layer fragmentation of the support and the resulting time-dependent accessibility of the monomers to the center of a catalyst is valid (Figure 1). DSC studies were performed in order to exclude the possibility of different polymers interpenetrating after formation (see the Supporting Information). Two thermal transitions were observed, and were in the same range as measured for the two PPs obtained in separate experiments with MBI or MCP. It is therefore clear that two types of PP, which are not mixed at the molecular level, are formed. If this were not the case, a single thermal transition would be expected. In principle, such a demixing could also occur because of the known immiscibility of PPs with different molecular weights; however, temperatures above the glass transition and the use of additives are required for such processes.[13]

A final proof of the core–shell morphology could not be established by using SEM, as atactic and isotactic polypropylene cannot be distinguished by using this method. TEM was also not successful for this purpose. However, further evidence was obtained by comparison of the products' surface morphology. Particles obtained from catalysts with MBI loaded in the shell and MCP in the core and vice versa were investigated by SEM. In the first case, a very rough surface that arises from the crystalline regions of the isotactic PP was observed (Figure 8a). In contrast, when MCP was immobilized in the outer layer, a very smooth particle surface that arises from the amorphous atactic PP was detected (Figure 8c). These surface morphologies were almost identical to the corresponding control experiments that used only one catalyst (Figure 8b,d); however, deep cavities, which arise from mechanical stress that causes a fragmentation of the core by the growing polymer, were observed in the mixed systems (SEM pictures for other systems are shown in the Supporting Information).

The activities of the two different core–shell systems depend not only on the polymerization temperature and time,

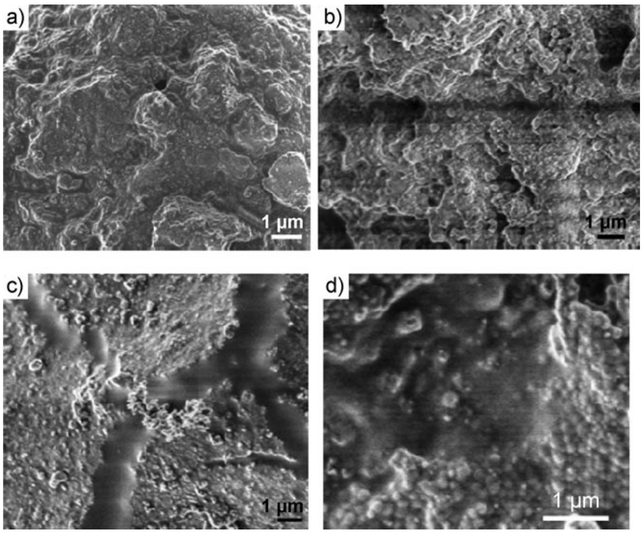

Figure 8. SEM images of product particles with catalysts loaded in different layers. a) MCP core and MBI shell, b) MBI shell only, c) MBI core and MCP shell, d) MCP shell only.

but also on the spatial resolution of the metallocenes. The activities vary from 170 kg mol^{-1} to 2100 kg mol^{-1} (Table 1) and thus reflect the progress of support fragmentation. Remarkably, the activities of the systems with MBI in the shell were always about 2.5 to 4 times lower than those for MCP. It is assumed that MBI formed a crystalline shell of isotactic PP that hampers the diffusion of the monomer into the core and slows down the polymerization process.[10]

Table 1: Activities of the core–shell systems.[a]

Catalytic system	Activity [kg mol^{-1}]			
	1 h 70 °C	3 h 70 °C	1 h 50 °C	3 h 50 °C
Core MCP/Shell MBI	190	530	170	300
Core MBI/Shell MCP	720	2100	460	1200

[a] Activities reported for the polymerizations of propene at 4 bar. See the Supporting Information for calculations of the support efficiency.

While core–shell particles are almost exclusively produced via emulsion using radical polymerization, we have presented a method for producing core–shell particles by catalytic polymerization. In this process, core–shell polymer particles are accessible in a single polymerization step by an appropriate catalyst setup with a complex architecture of the inorganic–organic hybrid support. This approach does not use self-assembly or compatibilization effects of amphipolar or immiscible polymers for structuring. Instead, we have introduced the spatially resolved loading of different polymerization catalysts as a technique for controlling the morphology of polymers in a blend. The support acts as a template for the final morphology. This method allows variation of a number of parameters: 1) the ratio of the thickness of the polymers layers can be controlled by the amount of catalyst in each layer, 2) the size of the particle is tunable by the reaction time and temperature, and the gas pressure, and 3) the glass transition temperature, as well as tacticity and molecular weight, can be optimized by the proper choice of the catalyst.

Spatially resolved loading of catalysts is, in principle, an approach suitable for all catalysts that polymerize olefins. In addition to core–shell structures, such a stepwise construction should also be applicable to other biphasic systems, such as sub-micrometer coated planar surfaces. By selective loading with catalysts or initiators, nano- or microstructured polymer-coated surfaces should be directly accessible during the polymerization.

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