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MODIFIED POLYPROPENES VIA METALLOCENE CATALYSIS

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MODIFIED POLYPROPENES VIA METALLOCENE CATALYSIS

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ABSTRACT

The copolymerization of propene with 1-olefins and other comonomers via metallocene catalysis is an important key to polymeric materials with a great variety of properties. The random incorporation of different side chains into the polypropene backbone gives access to a broad spectrum of properties of the polypropene materials ranging from thermoplastics across thermoplastic elastomers to olefin rubber which can be tailored using metallocene catalysts. With a lot of different 1-olefins it is possible to synthesize both copolymers of every desired composition as well as poly-1-olefins. Molecular, thermal, and mechanical properties of propene copolymers are determined by type and amount of the comonomer. The use of metallocene catalysis for the copolymerization of propene and cyclic olefins allows the incorporation of the cyclic olefin without ring opening reactions. This provides the way to a synthesis of copolymers with varying content of the cyclic olefin and interesting material properties. Polypropene graft copolymers used as single materials or acting as compatibilizer in polyolefin blends are very attractive polymeric products. Furthermore, via metallocene catalysis it is possible to synthesize polypropene-graft-polystyrene or polypropene-graft-polyisobutene. The method of synthesis as well as certain applications of such materials will be the main focus of this report.

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INTRODUCTION

During the last years, a new type of subject in polymer research can be observed. In the 7th and 8th decade of our century, the use of more and more special monomers in polymerization was the aim of the development of new polymer materials. Nowadays, the research in polymer science is more and more focused on the traditional, main polymers, whereas not the diversity of the monomers, but the adjustability of the product properties by combination of well-known monomers is placed into the center of research. The exclusive development of polymers by using "exotic" monomers was replaced by a quick development of chemical engineering with new catalytic systems and initiators for a controlled polymerization of monomers which have been known for a very long time [1, 2].

At present, metallocenes are establishing as a new generation of catalysts for the polymerization of ethene and 1-olefins. Characterized by uniform catalytic centers ("single-site" catalysts), a high polymerization activity and the possibility of controlling molecular weight and comonomer incorporation, these catalysts allow the synthesis of novel polyolefin materials with tailored properties [3, 4].

Polyolefins synthesized by metallocene catalysis show a narrow molecular weight distribution compared to conventional catalysts of the Ziegler-Natta type (Figure 1). Furthermore, metallocene catalysts provide copolymers with a

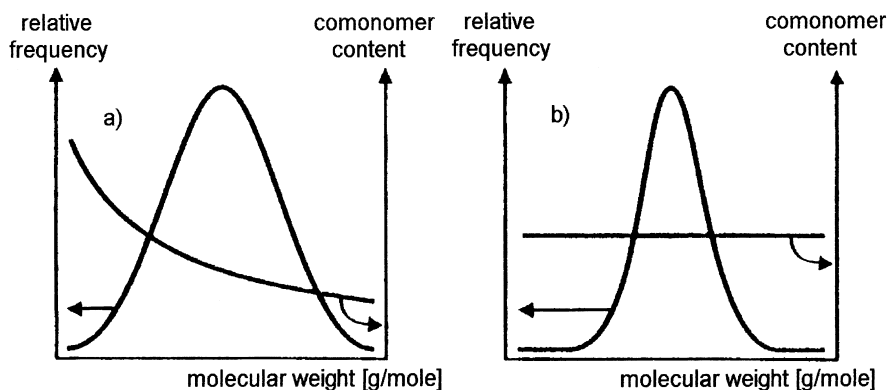


Figure 1. Comparison of metallocene and Ziegler-Natta catalysts in molecular weight distribution and comonomer incorporation [6].

random distribution of the comonomer into the growing polymer chain. Another reason for the success of metallocenes that should not be underestimated is the possibility of the employment of this catalytic systems in existing production processes (“drop in technology”) [5].

Due to the broad variation of material properties in connection with a good processability and low material costs polypropene is one of the most expanding polymeric materials in the present time. In the last decade, the consumption of this polymer was rising all over the world above-average. Between 1994 and 2000 the growth rate of polypropene consumption is valued at approximately 9% p.a. (Figure 2) [7]. Hence, it is predicted that polypropene will be advancing to the mostly consumed polymeric material [8].

An important reason for the continual increase in the consumption of polyolefins is the possibility of the manufacture of novel materials by employing metallocene catalysts. Thus, by metallocene catalysis copolymers of cyclic olefins [9], syndiotactic [10] or elastomeric polypropene [11] can be achieved for the first time in plant scale. A further advantage of polyolefins is their non-polluting manufacture. From an ecological point of view, polyolefins are very attractive products due to the possibility of the reduction of polyolefins by hydrogenolysis. Thus, in a recycling process, the long polymeric materials might be transformed into short olefins [12, 13].

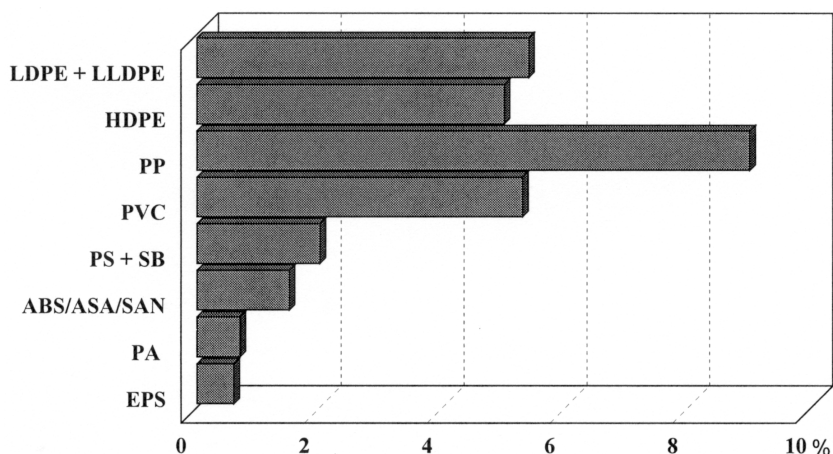


Figure 2. World-wide consumption growth rate of polymeric materials.

This report will give a short review about some activities of our team in the synthesis of novel polyolefin materials with a broad range of properties. Correlations between structure of polymers and properties will be given.

Homopolymerization of 1-Olefins

A lot of publications dealing with the homo- and copolymerization of ethene and propene [1, 14-17] via metallocene catalysis have been made. Some highlights in modern research are the synthesis of long chain branched polyethene [18, 19], elastomeric polypropene [20-23] as well as the living polymerization of propene or other 1-olefins by metallocenes [24, 25]. Furthermore, the use of supported metallocenes for existing production processes is also a present research topic, [26, 27].

Since the mid-80's, the development of metallocene catalysts allows the synthesis of a broad range of polymers with different chain conformations. This is demonstrated for polypropene in Figure 3.

The list of monomers which can be polymerized by metallocene catalysts today includes numerous 1-olefins or dienes as well as aromatic compounds, cyclic olefins or other monomers, e.g. methyl methacrylate or carbon monoxide [34-36].

Our group at the Martin-Luther-University Halle-Wittenberg investigated the homo- and copolymerization of 1-olefins for some years [37-39]. Higher linear 1-olefins up to 1-eicosene as well as branched 1-olefins, e.g., 4-methylpentene-1 were used for polymerization experiments. The variation of the metallocene catalyst used for such polymerization experiments is the origin for the synthesis of poly-1-olefins with a broad range of properties. Results of the polymerization of 1-olefins from propene up to 1-eicosene by different metallocenes are reviewed in Table 1.

The comparison of a similar zirconocene and a hafnocene catalyst shows that the hafnocene catalyst produces polymers with higher molecular weight. In both series, the values of the molecular weight distribution are ranging from 1,5 to 2,5 typical of metallocenes.

By the characterization of the thermal properties of the poly-1-olefins obtained a decrease in the glass transition temperatures with growing length of the 1-olefin used as monomer was observed. The glass transition temperature for homopolymers of 1-olefins with more than 10 carbon atoms could not be detected by differential scanning calorimetry.

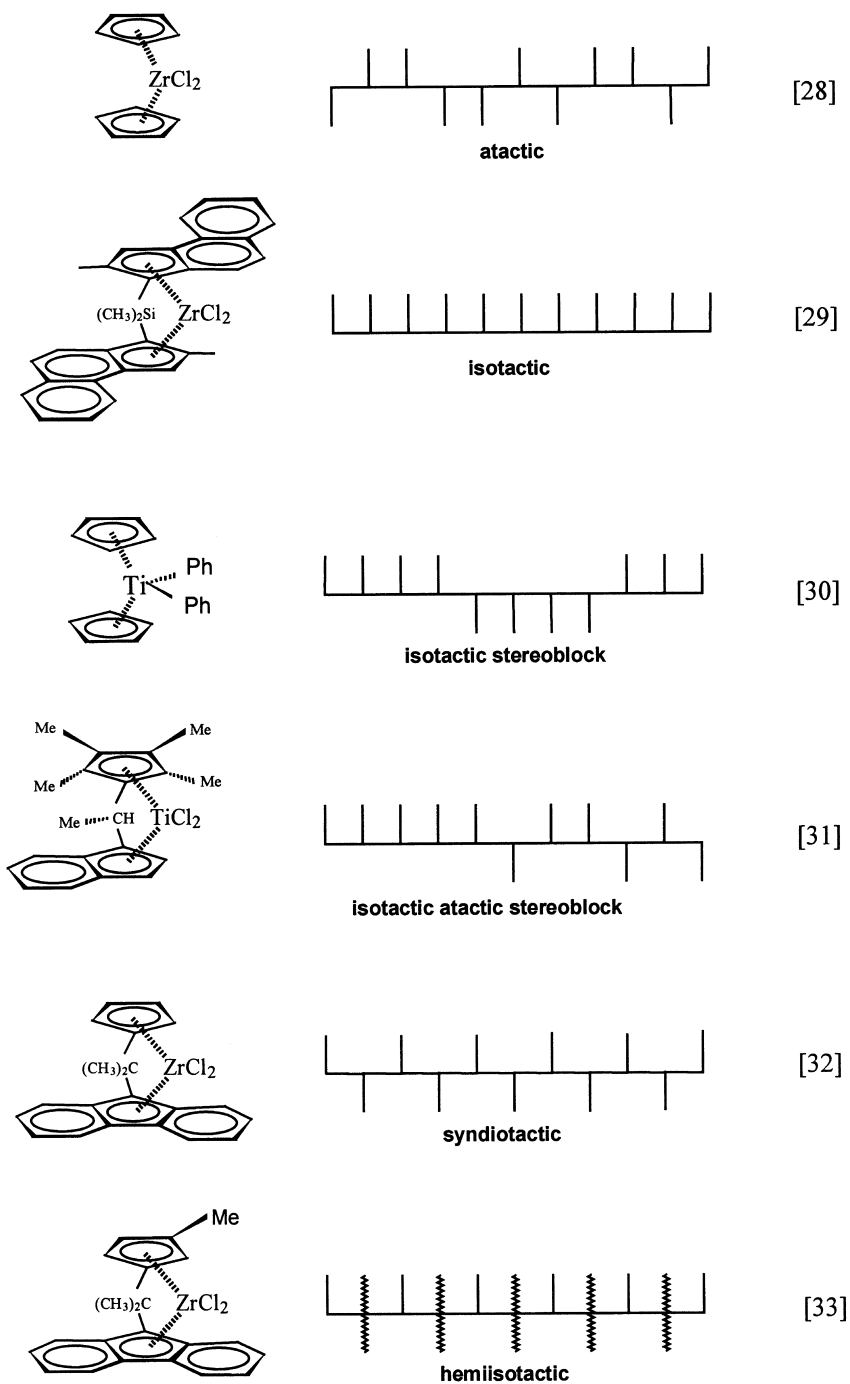
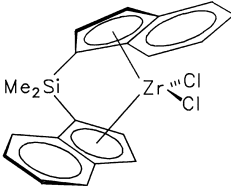
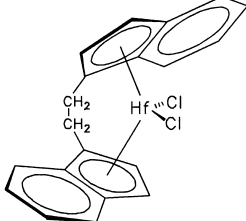


Figure 3. Relationship between the structure of metallocene and polymer chain.

TABLE 1. Polymerization of 1-Olefins by Different Metallocene Catalysts

| Metalocene |  | | | | |  | | | | |
|----------------------|---|----------------------------|-------|------------------------|-------------------------|--|----------------------------|-------|------------------------|-------------------------|
| | 1-Olefin | M _w (kg/mol) | D | T _g (°C) | T _{m1} (°C) | T _{m2} (°C) | M _w (kg/mol) | D | T _g (°C) | T _{m1} (°C) |
| Propene | 128 | 2.15 | -11.1 | 149.0 | - | 401 | 2.28 | -8.1 | 137.9 | - |
| Butene-1 | 29 | 2.26 | -15.6 | 110.7 | - | 107 | 2.01 | -26.5 | 80.5 | 87.9 |
| Pentene-1 | 34 | 1.56 | -33.2 | 68.0 | 74.0 | 84 | 1.78 | -37.0 | 62.5 | - |
| Hexene-1 | 37 | 1.52 | -45.2 | - | - | 95 | 1.75 | -47.6 | - | - |
| Octene-1 | 51 | 1.50 | -63.8 | - | - | 65 | 1.82 | -63.9 | - | - |
| Decene-1 | 45 | 1.78 | - | 12.5 | 31.7 | 67 | 1.6 | - | 13.0 | 28.0 |
| Dodecene-1 | 50 | 1.62 | - | 39.9 | 46.5 | 99 | 2.07 | -107 | 36.3 | 44.0 |
| Tetradecene-1 | 50 | 1.69 | - | 27.0 | 58.4 | 116 | 1.53 | - | 24.8 | 50.0 |
| Hexadecene-1 | 70 | 1.89 | - | 35.5 | 69.7 | 103 | 2.52 | - | 26.0 | 62.0 |
| Octadecene-1 | 68 | 1.85 | - | 43.1 | 74.9 | 70 | 1.94 | - | 37.0 | 68.0 |
| Eicosene-1 | 47 | 1.86 | - | 56.0 | 77.5 | 101 | 1.94 | - | 54.3 | 67.9 |

The melting behavior of poly-1-olefins synthesized via metallocene catalysis compared to conventional catalysts from Ziegler-Natta type is similar in principle [40]. From polypropene to polypentene-1, the melting point is decreasing, whereas from polydecene-1 to polyeicosene-1, the melting points are increasing. Polyhexene and polyoctene are completely amorphous polymers at room temperature without any detectable melting point. It is worth mentioning that for higher homopolyolefins two melting points were obtained. This could be an indication of side chain crystallinity. Some DSC heating curves for polyolefins are shown in Figure 4.

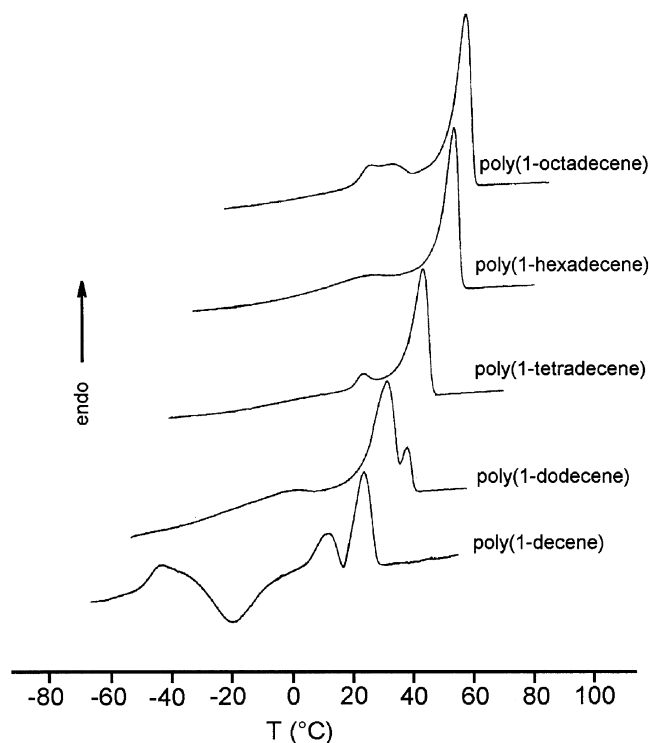


Figure 4. DSC heating curves for poly-1-olefins obtained from the metallocene catalyst $\text{Et}[\text{Ind}]_2\text{HfCl}_2$.

Propene/1-Olefin Copolymers

The variation of the chain structure of polyolefines such as polyethene and polypropene is important to a conscious modification of their mechanical properties.

In polyethene production, the copolymerization of ethene with low amounts of α -olefines leads to linear low density polyethene (PE-LLD). The market of this PE-LLD is large and expanding [41]. In 1997, the production capacities all over the world had been run to more than 12 thousands of metric tons p.a. [42]. Typical comonomers used are propene, butene-1, pentene-1, hexene-1, octene-1 [43] and 4-methyl-pentene-1 [44].

Heterogeneous Ziegler-Natta catalyst owns a lot of different active centers [45] and, for this reason, cannot produce random copolymers. In contrast to this fact, homogeneous catalysts based upon metallocenes activated with methy-

luminoxanes [46] or other cocatalysts [47] open new prospects to the synthesis of new polymers with narrow molecular weight distribution and uniform copolymer compositions. These systems give rise to the production of homopolymers as well as copolymers with random comonomer distribution and an excellent activity at lower temperatures [48].

The great industrial interest on metallocenes is based on the possibility of applying these catalysts in existing modern processes [49]. One way to modern metallocene “drop in” catalyst technology is a heterogenization of these catalyst systems, which enables good control of the polymer morphology [50, 51] in gas-phase process.

In a solution process, the homogeneous metallocene catalysts combined with methylaluminoxane is now used commercially to produce ethene/octene-1 copolymers. The products obtained with these “constrained geometry catalysts” are LLDPE and plastomers [52].

The new developments in catalyst technology are also used in polypropylene applications.

By the means of different 1-olefins in copolymerization with propene it is possible to obtain various polymeric structures (Figure 5).

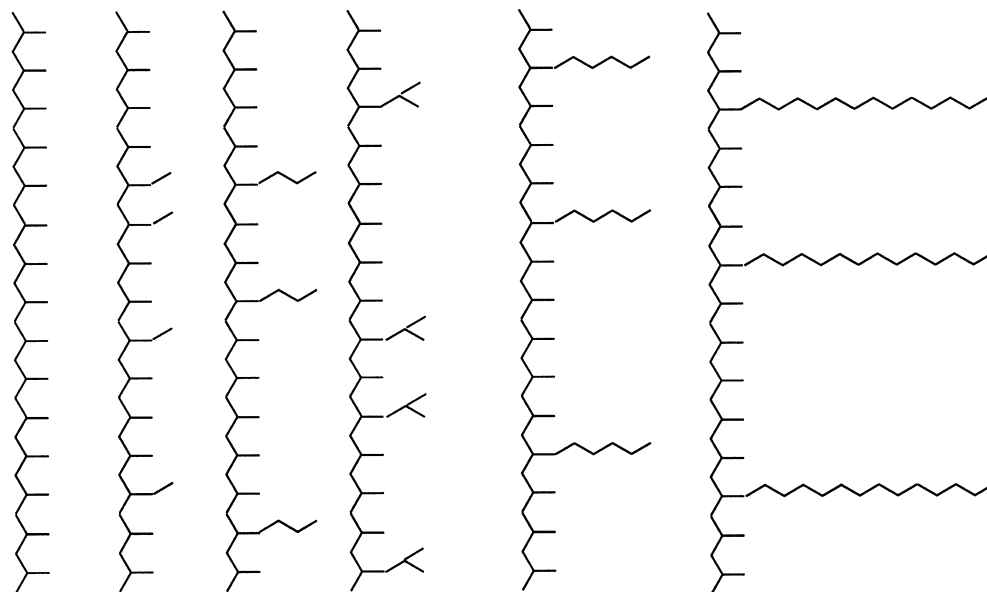


Figure 5. Polymer structures available by use of different metallocene catalysts.

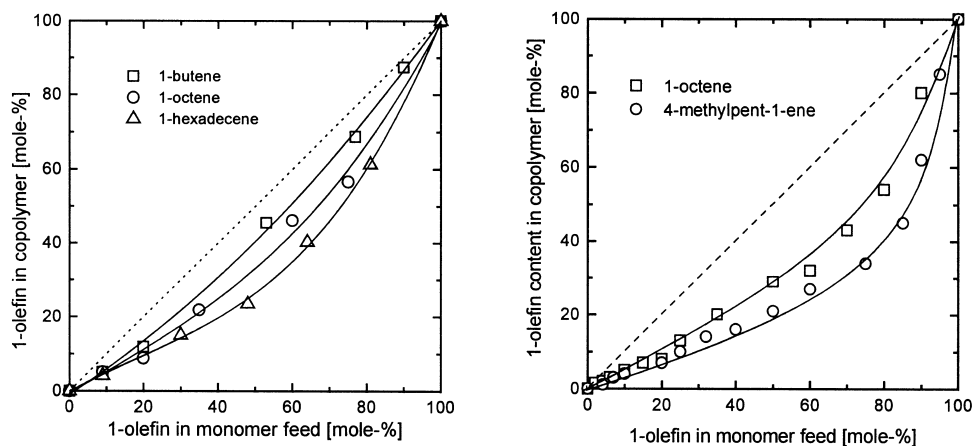


Figure 6. Copolymerization diagram for some propene/1-olefin copolymers by using the metallocene catalysts $\text{Et}[\text{Ind}]_2\text{HfCl}_2$ (left) and $\text{Me}_2\text{Si}[\text{2-Me-BenzInd}]_2\text{ZrCl}_2$ (right) and methylaluminoxane as cocatalyst.

The copolymerization of propene and different 1-olefins including the linear butene-1, hexene-1, octene-1, dodecene-1 and hexadecene-1, as well as the branched 4-methyl-pentene-1 were investigated by our group [37, 38]. The copolymerization diagram for such copolymerizations is shown in Figure 6. A good incorporation of the most comonomers used into the growing polymer chain can be observed.

Metallocene catalysts give rise to the synthesis of copolymers in the entire composition range from polypropene up to poly-1-olefin. With hafnocene as the catalyst in copolymerization of propene and higher 1-olefins, a decrease in reactivity was found when the length of the 1-olefin was increased. When branched 1-olefins such as 4-methyl-pentene-1 was used as comonomer in copolymerization with propene, a good incorporation was observed.

In Figure 7 and Table 2, the reactivity parameters of several propene/1-olefin copolymerizations are listed. These parameters describe the reactivity of the monomers used in the copolymerization. For propene/1-olefin copolymerization via metallocene catalysis a random distribution of the comonomer units in the copolymer can be obtained.

The determination of the copolymerization parameters can be performed in different ways. One is based on ^{13}C -NMR measurements by analyzing the

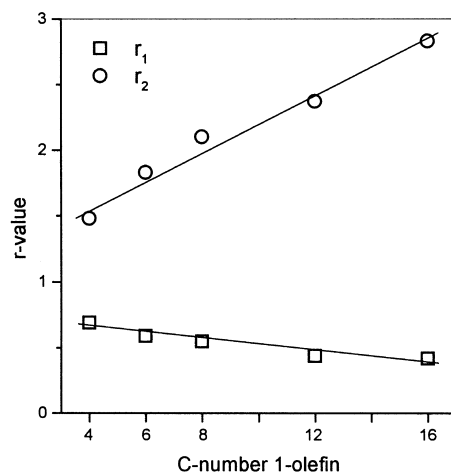


Figure 7. Copolymerization parameters for propene/1-olefin systems.

diads of the methylene carbon atoms [53]. In Figure 8, a ^{13}C -NMR spectrum of a propene/octene-1 copolymer is presented. The carbon atoms necessary for the determination of the reactivity parameters are C-10, C-1, and C-12.

An important measuring device for the characterization of polymers is the differential scanning calorimetry (DSC). There, the thermal behavior of polymers can be detected. In Figure 9, several DSC heating curves of propene/octene-1 copolymers are drawn. It can be observed, that the increase in the comonomer content of the polymer leads to a decrease in the melting point.

TABLE 2. Reactivity Parameters of Several Propene/1-Olefin Copolymerizations

| Comonomer | r ₁ | r ₂ | r ₁ •r ₂ |
|--------------|----------------|----------------|--------------------------------|
| Butene-1 | 1.48 | 0.69 | 1.02 |
| Hexene-1 | 1.83 | 0.59 | 1.08 |
| Octene-1 | 2.10 | 0.55 | 1.16 |
| Dodecene-1 | 2.37 | 0.44 | 1.04 |
| Hexadecene-1 | 2.83 | 0.42 | 1.18 |

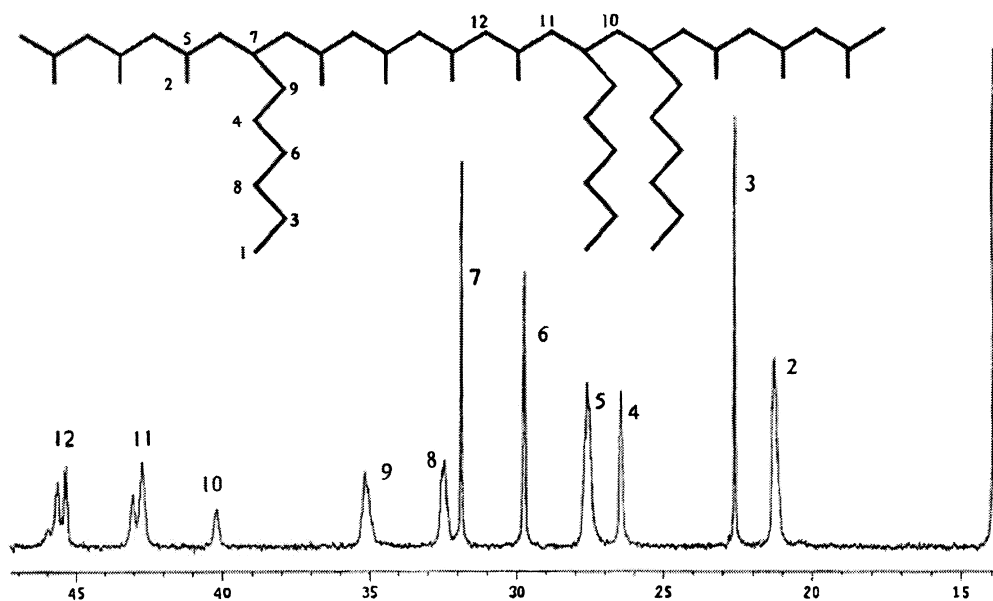


Figure 8. ^{13}C -NMR spectrum of a propene copolymer including 29 mol% octene-1.

The peak area, which describes the part of the crystalline regions in the polymer, is also decreasing. A reduction of the crystallinity by the incorporation of higher 1-olefins is typical of propene copolymers.

The melting points of several propene copolymers obtained via metallocene catalysis are demonstrating, how the crystallizability is drastically

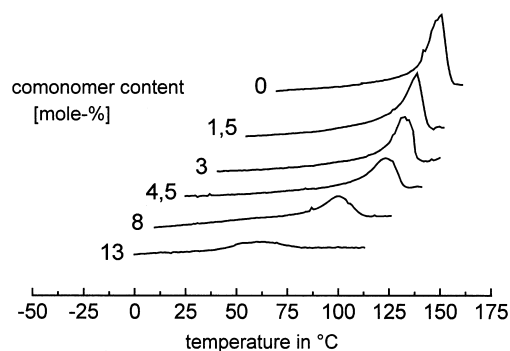


Figure 9. DSC-heating curves for propene/octene-1 copolymers.

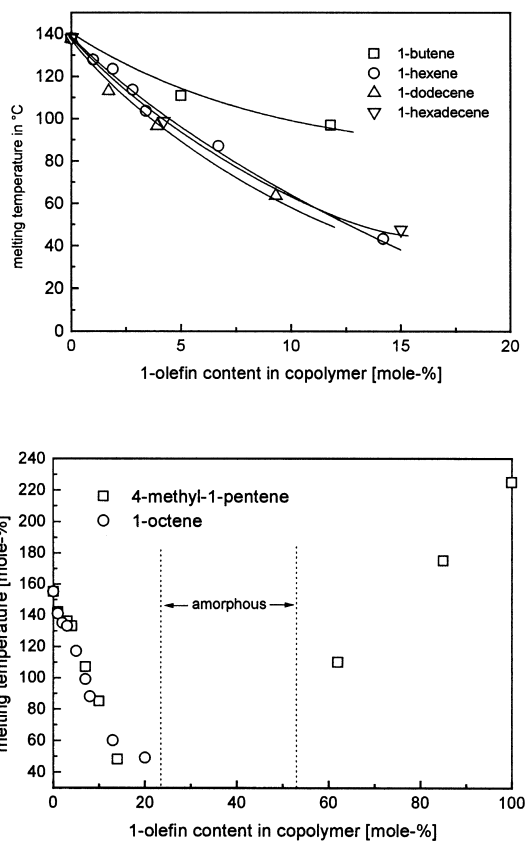


Figure 10. Melting behavior of propene/1-olefin copolymers.

depending on 1-olefin incorporated (Figure 10). Usually, the incorporation of more than 15 mol% 1-olefins leads to amorphous polymers. However, a completely different behavior is observed in the copolymerization of propene and 4-methyl-pentene-1.

Since, poly-4-methyl-pentene-1 is a semi-crystalline polymer [54, 55], propene copolymers with a high amount of 4-methyl-pentene-1 also show semi-crystalline behavior. So, increasing melting points were found for copolymers with more than 60 mol% 4-methyl-pentene-1 incorporated by using the metallocene catalyst $\text{Me}_2\text{Si}[2\text{-Me-BenzInd}]_2\text{ZrCl}_2$. The melting points increased up to 225°C for the homopolymer.

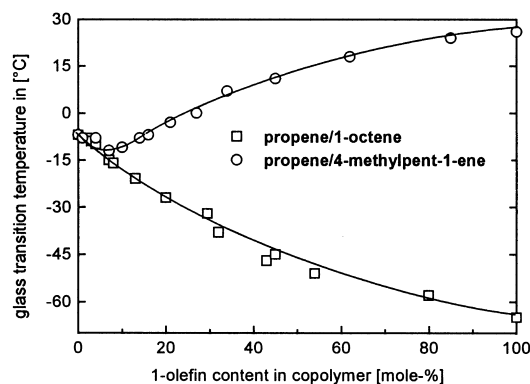


Figure 11. Glass transition temperatures of propene copolymers.

Furthermore, DSC measurements give information about the glass transition of polymers. The variation of the glass transition temperature nearby -10°C for pure polypropene is important for the applications of propene polymers. The incorporation of 1-olefins into the polypropene chain using metallocene catalysis is one successful way for a defined regulation of their thermal properties. In Figure 11, the glass transition temperatures of propene/octene-1 and propene/4-methyl-pentene-1 copolymers as a function of the comonomer incorporation are compared. The insertion of octene-1 leads to a constant decrease in the glass transition temperature of the propene copolymers. In contrast to it, the result of the incorporation of a higher amount of 4-methyl-pentene-1 into the growing polymer chain is an increase in the glass transition up to 25°C for the pure poly-4-methyl-pentene.

The dependence of the mechanical properties on the comonomer content was investigated by the determination of tensile properties. Figure 12 gives the stress-elongation curves of some propene copolymers.

The modulus of elasticity of semi-crystalline polymers dependent on the range of crystallinity. A result of a decreasing crystallinity is a sinking modulus of elasticity in tension. By incorporation of a low content of octene-1 or 4-methyl-pentene-1 the variation of the modulus ranging from nearly 2000 N/mm^2 down to 200 N/mm^2 is possible. Incorporation of octene-1 and 4-methyl-pentene-1 gives copolymers with comparable modulus of elasticity.

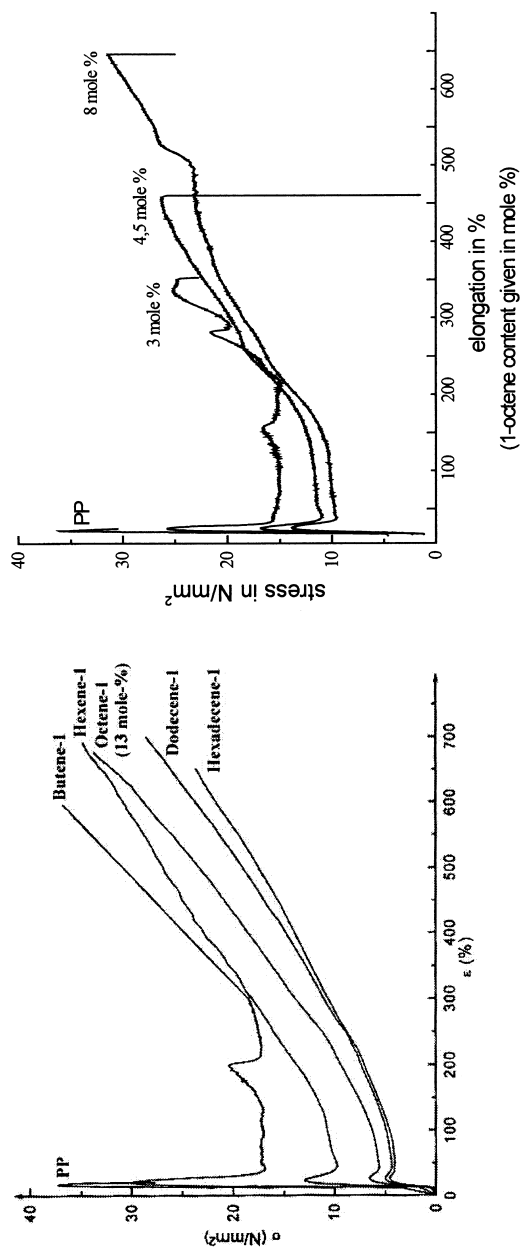


Figure 12. Stress-elongation curves of selected propene copolymers.

Another property of the copolymers depending on the comonomer incorporation is the elongation at break. The incorporation of a lowest content of 1-olefin into the polypropene chain creates products with a drastic increased stretchability. Pure polypropene is only stretchable for 3%. The elastic limit of the copolymers is rising up to 600 %.

A decrease in tensile stress with a higher comonomer content incorporated is observed.

In consideration of the mechanical properties, the copolymers obtained are attached to the class of plastomers. The crystallinity still existing within the chain leads to the possibility of a thermoplastic processing of the materials. The disturbance of this crystallinity by the incorporated comonomer units yields copolymers with rising elastomeric properties.

Copolymerization of Propene and Cyclic Olefins

An example for a completely new class of polyolefins which are available by metallocene catalyst development is the polymerization and copolymerization of cyclic olefins [56-58]. Products obtained are described as COC (cyclic olefin copolymers). Metallocene catalysts can polymerize these olefins without ring opening reactions. Homopolymers of cyclopentene and norbornene are extraordinary high melting polymers with a very good resistance to chemicals [59]. The result of copolymerization of ethene and norbornene is a material with a high transparency and a very good heat stability [60]. Nowadays, ethene-norbornene copolymers called as Topas® (thermoplastic olefin polymers of amorphous structure) are offered by the industry [61].

In Figure 13, structures of propene copolymers with cyclic olefins available via metallocene catalysis are shown.

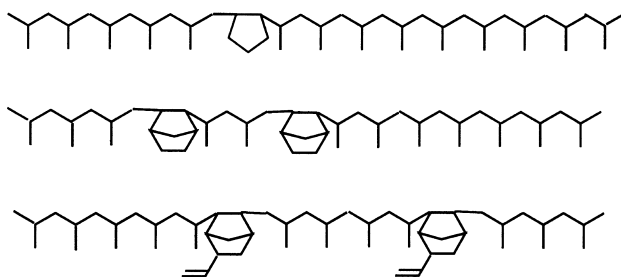


Figure 13. Polymer structures of some propene copolymers with cyclic olefins.

Investigations of the copolymerization behavior of cyclic olefins in the copolymerization with propene were carried out by our group [62, 63]. A strong influence of the incorporation behavior on the structure of the cyclic olefin used for such copolymerization experiments can be observed. While in copolymerization of propene with the monocyclic cyclopentene, the comonomer is really incorporated only when used in a high surplus in monomer feed, the bicyclic olefins norbornene and vinylnorbornene show a good insertion into the growing polypropene chain (Figure 14).

Remarkably, vinylnorbornene is only incorporated into the polymer chain via the endocyclic double bond. The exocyclic double bond of the comonomer is not attacked and can be used for further modification reactions [64].

All the cyclic olefins used in copolymerization experiments with propene have one thing in common: A higher incorporation of the comonomer leads to a drastic decrease in the polymerization activity and molecular weight. Nevertheless, copolymers of every desired composition can be obtained by varying the monomer ratio.

A result of the incorporation of cyclic olefins is a higher chain rigidity than can be detected by the investigation of the glass transition temperature of

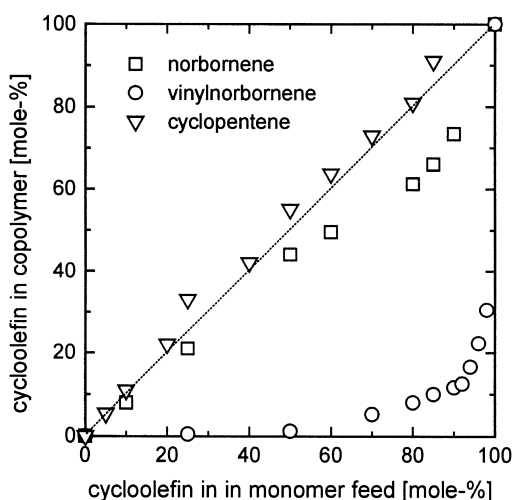


Figure 14. Copolymerization of propene and cyclic olefins.

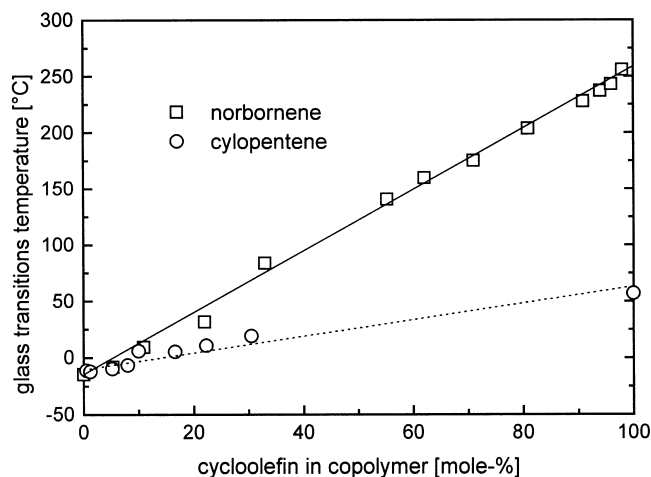


Figure 15. Glass transition temperatures of the system propene/cyclic olefin.

these copolymers (Figure 15). By using cyclic olefins in metallocene catalyzed propene copolymerization, it is possible to synthesize polymeric materials with adjustable glass transition temperature ranging from -10°C up to 225°C .

Polypropene Graft Copolymers

The property range of polypropene can be broadened by a chemical modification or by physically blending polypropene with other polymers [65, 66]. Because of the incompatibility of the components in most of the polypropene blends graft copolymers with polypropene backbone and chemically different side chains that can be used as compatibilizers are attractive products [67]. Compatibilization with graft structures can be achieved reactively by the coupling of reactive groups on each of the immiscible polymers or by the addition of premade polymers [68, 69].

Poly(propene-g-styrene) graft copolymers (PP-g-PS) were prepared by free radical polymerization of styrene onto polypropene in solid phase, and it provided an optimum fine dispersion and phase stability of polypropene/poly-styrene blends [70, 71]. However, side reactions can occur in these modification processes. Therefore, it is difficult to control and characterize the structure and composition of such copolymers [72, 73]. For a better understanding of the com-

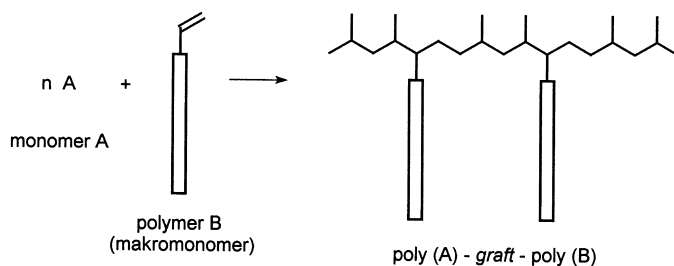


Figure 16. Synthesis of graft copolymers by using the macromonomer method.

patibilization process and the influence of molecular parameters of the compatibilizer on morphology and mechanical properties of polypropene blends it is necessary to use well-defined structures as a compatibilizing agent. The macromonomer method (Figure 16) is a versatile synthetic route for obtaining defined graft copolymers [74].

On the basis of these findings, we intended to investigate the application of the macromonomer method in polyolefin chemistry, i. e. the possibility to copolymerize olefins with macromonomers using metallocene catalysts. Based on the experiences about the copolymerization of propene with norbornene, a synthetic pathway for the copolymerization of propene and norbornenyl terminated polystyrene macromonomers was created. This route included the synthesis of 5-chloromethylbicyclo[2.2.1]heptene-2 [75] as precursor for the anionic polymerization of styrene. One of the most attractive 1-olefin-terminated macromonomer is 1-propenyl-terminated polyisobutene (PIB) [76] which is easily available by quasiling [77, 78] carbocationic polymerization of isobutene [79-82]. This rubbery polymer with its fully saturated structure provides a non-reactive backbone and outstanding thermal, oxidative and radiation stability.

For the copolymerization of propene with the polyisobutene and polystyrene macromonomers, we used a metallocene catalyst derived from the reaction of $[\text{Me}_2\text{Si}(2\text{-Me-4,5-Benzind})_2]\text{ZrCl}_2$ with methylaluminumoxane. This catalyst was selected because of the better accessibility of the active center for long 1-olefins in the benzindenyl system compared to other highly active and highly isospecific metallocenes with indenyl ligands that are substituted in the 4-position with isopropyl, phenyl or naphthyl groups [17]. The results of some copolymerization reactions are summarized in Table 3.

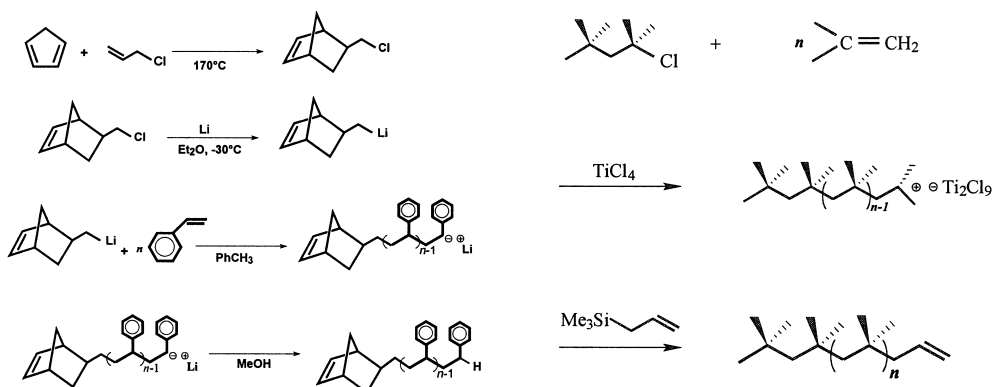


Figure 17. Synthesis of norbornenyl terminated PS- and allyl-terminated PIB-macromonomers.

The characterization of the graft copolymers was carried out by the gel-permeation chromatography (GPC) at 135°C in 1,2,4-trichlorobenzene as eluant. Figure 19 shows the resulting GPC traces of PIB and the graft copolymers containing this macromonomer.

PP-g-PIB and PP-g-PS were extracted with *n*-hexane before GPC characterization. As can be seen in this example, the GPC curves of the graft copolymers PP-g-PIB exhibit a shape that is typical of metallocene polyolefins. Macromonomer rich fraction is not detectable as a shoulder neither in the low nor in the high molecular weight regions of the curves.

Mechanical properties and morphology of blends of isotactic polypropylene (PP) and atactic polystyrene (PS) were investigated with special interest in the compatibilizing effect of graft copolymers prepared by the macromonomer method, as can be seen in Figure 20. In blends with 80 wt% polypropylene and 20 wt% polystyrene, it was found that small amounts of the graft copolymers (1–2.5 wt%) are sufficient to cause a significant change in blend morphology and properties.

Young's modulus and tensile strength increase with the addition of the graft copolymer while elongation at break decreases. Morphology studies show that there is a strong effect of the graft copolymer concentration on the compatibilizing efficiency. Only 1 wt% of graft copolymer added causes a much better dispersion of the polystyrene domains in the polypropylene matrix. An increase in

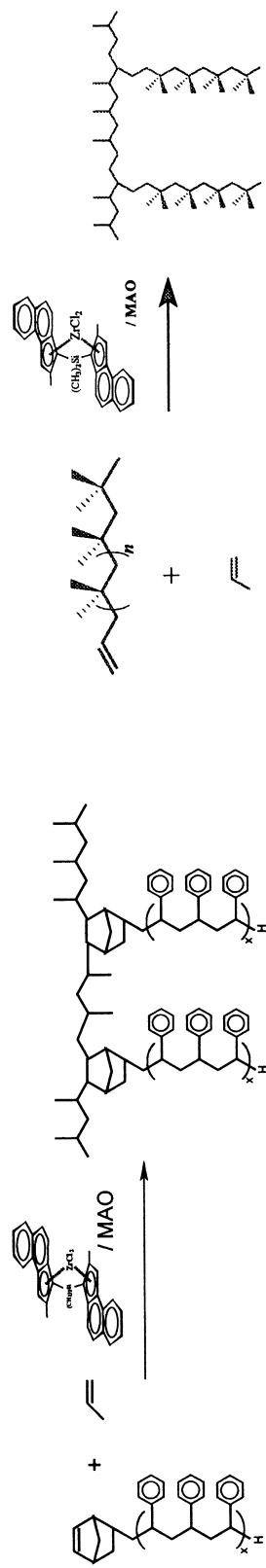


Figure 18. Copolymerization of propene with PS- (left) and PIB-macromonomers (right).

TABLE 3. Copolymerization of Propene with Several PS- and PIB-Macromonomers 890

| macromonomer | | | | Polypropene graft copolymer | | | |
|--------------|----------------|--------------------------------|----------------|------------------------------|----------------|-----------------------------|----------------|
| Type | M _w | M _w /M _n | T _g | macro- monomer content | M _w | branches per molecule | T _m |
| | (kg/mole) | | (°C) | (wt-%) | (kg/mole) | | (°C) |
| PIB | 2.5 | 1.09 | -81 | 10.9 | 31 | 0.85 | 123 |
| | 9.8 | 1.19 | -70 | 13.5 | 15 | 0.11 | 131 |
| PS | 0.8 | 1.10 | 8 | 31.6 | 6.2 | 2.5 | 106 |
| | 4.9 | 1.08 | 92 | 53.7 | 31 | 3.4 | 126 |
| | 11.5 | 1.17 | 96 | 72.4 | 51 | 3.2 | 126 |
| | 18.5 | 1.03 | 99 | 68.9 | 34 | 1.3 | 122 |

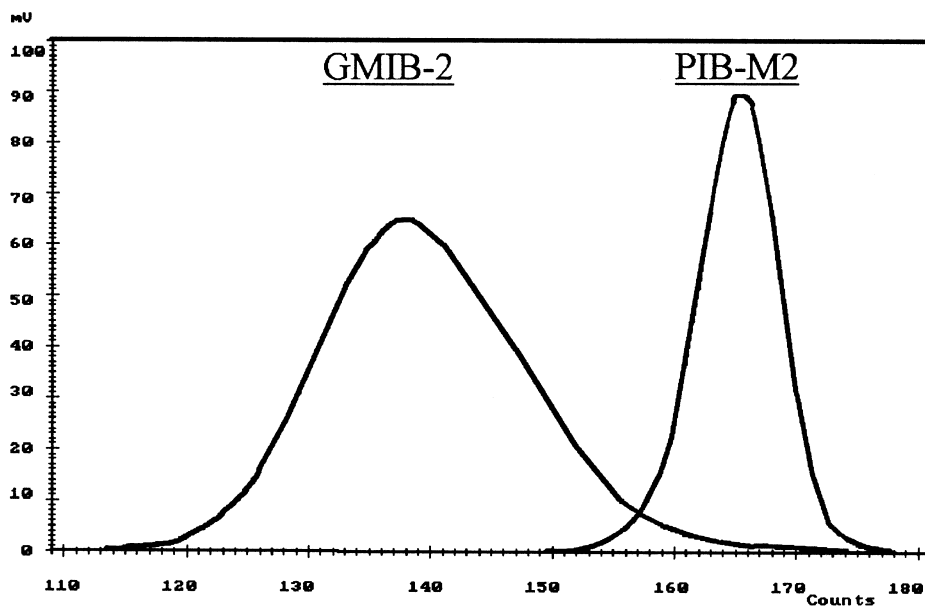


Figure 19. GPC curves of PP-g-PIB GMIB-2 and the starting macromonomer PIB-M2.

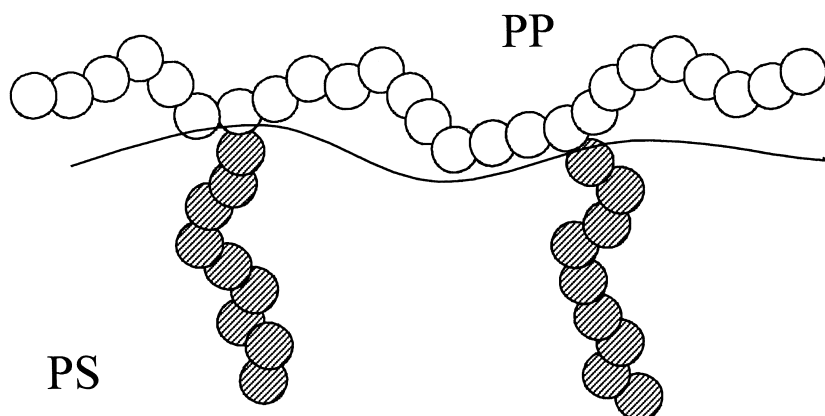


Figure 20. PP-g-PS as compatibilizer in PP/PS blends.

the compatibilizer concentration leads to significantly better phase adhesion between the immiscible blend components. Furthermore, a remarkably influence of the molecular weight and number of grafts on the morphology and mechanical properties can be observed.

CONCLUSION

The aim of this report was to review some possibilities of synthesis of polyolefin materials with adjustable properties by metallocene catalysis. In consideration of their mechanical properties such polymers could find applications in the field of thermoplastic polyolefins, thermoplastic elastomers, and polyolefin rubbers.

Because of the broad range of properties polypropene materials obtained via metallocene catalysis will play a very interesting role in the commercial plastic world and how today we can observe polymeric materials based on ethene copolymers. The use of versatile catalytic systems such as metallocenes is one important key to opening the door to the novel tailor-made polypropene materials.

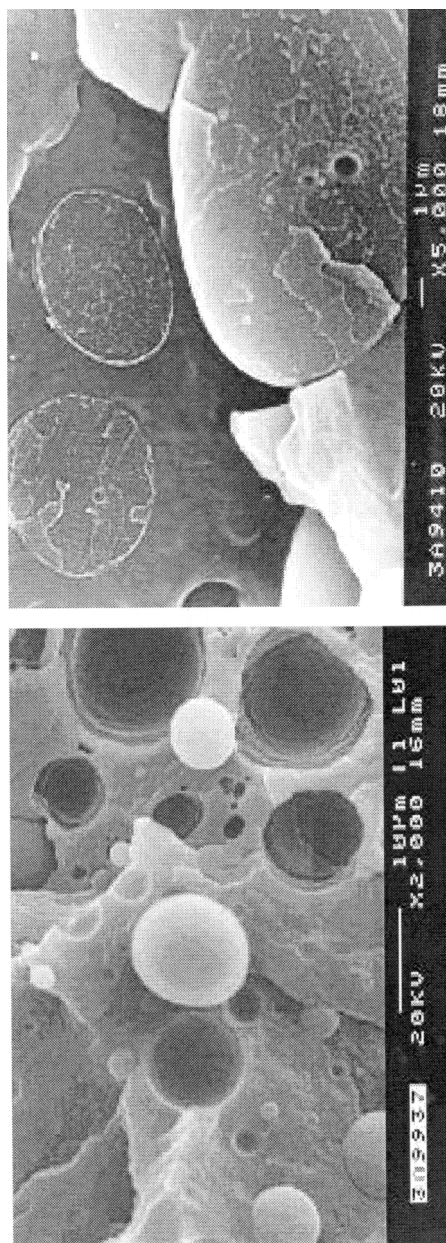


Figure 21. Electron microscopy investigation of PP/PS blends.

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