

P O L I M E R Y

MIESIĘCZNIK POŚWIĘCONY CHEMII, TECHNOLOGII i PRZETWÓRSTWU POLIMERÓW

OD REDAKCJI

Niniejszy zeszyt czasopisma „Polimery” jest w większości poświęcony tematyce poliolefinowej — zagadnienia tego dotyczy 6 pierwszych artykułów. Za inicjatywę wydania takiego zeszytu, liczne i czasochłonne kontakty z autorami oraz twórczą pomoc związaną z przygotowaniem materiałów do druku zespół redakcyjny przekazuje serdeczne podziękowania Pani Profesor Marii Nowakowskiej z Uniwersytetu w Opolu. Pragniemy również gorąco podziękować Pani Profesor Krystynie Czaji — z tejże Uczelni — która brała czynny udział w recenzowaniu i ostatecznym przygotowaniu materiałów do druku.

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Long — chain branched polypropylenes obtained by copolymerization with use of metallocene catalysts

Summary — Metallocene/methylalumoxane catalysts can be used to synthesize macromonomers of ethylene as well as copolymers of propene with macromonomers. In the experiments $\text{Me}_2\text{C}(\text{Cp})_2\text{ZrCl}_2$ is used which let polymerize ethylene to macromonomers but is unable to cause propene polymerization. After addition of $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ and propene, long chain branched polypropylenes are produced with isotactic, syndiotactic or atactic backbone. The differences of crystalline or amorphous polypropylene backbone with crystalline polyethylene side chains were investigated. It was shown that the melting temperature (T_m) decreases strongly with increasing concentration of macromonomers in the copolymers. To reduce the melting point by 20 °C 0.1 mol. % of macromonomers is sufficient.

Key words: metallocene catalysis, copolymerization, polypropylene, branched polymers, macromonomers.

DŁUGOŁAŃCUCHOWE ROZGAŁĘZIONE POLIPROPYLENY OTRZYMANE W WYNIKU KOPOLIMERYZACJI WOBEC KATALIZATORÓW METALOCENOWYCH

Streszczenie — Katalizatory metalocenowe z metyloalumoksanem (MAO) zastosowano do syntezy makromonomerów etylenu, jak również do kopolimeryzacji propenu z makromonomerami. Polimeryzację etylenu, prowadzącą do otrzymania makromonomerów, katalizowano za pomocą $\text{Me}_2\text{C}(\text{Cp})_2\text{ZrCl}_2/\text{MAO}$ [wzór (I)]. Następnie otrzymane makromonomery kopolimeryzowano

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z propenem używając jednego z trzech typów katalizatorów metallocenowych [wzory (II)—(IV)], co pozwoliło uzyskać kopolimery izotaktyczne, syndiotaktyczne lub ataktyczne. Typ użytego katalizatora wpływa także na zdolność do wbudowywania makromonomerów w makrocząsteczkę kopolimeru oraz na masę molową (M_w) produktu. Użycie makromonomerów o większej M_w zmniejsza ich zawartość w kopolimerze, podobnie jak zmniejszanie zawartości propenu w mieszaninie reakcyjnej. Stwierdzono ponadto, że wzrost zawartości makromonomerów w kopolimerze istotnie zmniejsza jego temperaturę topnienia (T_m).

Słowa kluczowe: kataliza metallocenowa, kopolimeryzacja, polipropylen, polimery rozgałęzione, makromonomery.

Isotactic polypropylene is the commercial polymer widely used in the world because of its wide range of applications. In 2006, more than 40 million tons were produced. Further development is motivated by its probable applications in the industry to vary the microstructures to reduce the amounts of the material needed for tailored applications [1, 2].

Metallocene/methylalumoxane (MAO) catalysts are highly active and suitable for the production of precisely designed polyolefins and engineering plastics. Especially zirconocene complexes have opened frontiers in the area of new polymer syntheses and processing. By change of the ligand structure, these catalysts allow synthesize isotactic, isoblock, syndiotactic, stereoblock or atactic polypropylenes as well as new copolymers with superior properties such as film clarity, tensile strength and lower extraction efficiency [3—8].

In the past, copolymers of propene with long chain α -olefins were less investigated than the homologous ethylene copolymers. In recent years, there is observed greater interest in branched polypropylenes, too [9].

Low melt strength is required for industrial processes such as foaming, thermoforming or blow-melting [10]. Poon *et al.* [11] have analyzed the microstructure, morphology and mechanical properties of propene/hexene copolymers. Furthermore, Arnold *et al.* [12] reported the copolymerization of propene with higher α -olefins up to hexadecene in the presence of the $\text{Et}(\text{Ind})_2\text{HfCl}_2/\text{MAO}$ catalyst, and detected the effect of the side chain length. The analyzed copolymers show only a small effect of the different side chain lengths. Quijada *et al.* [13] synthesized iso- and syndiotactic copolymers with 1-hexene and 1-octadecene by different C_s - and C_2 -symmetric zirconocenes. Metallocene-catalyzed copolymers are chemically homogeneous and of narrow molecular weight up to large incorporation of comonomer.

In the past, we have studied the copolymerization of propene with hexacocene (C_{26}) using isotactic, syndiotactic or atactic working zirconocene/MAO catalysts. When the introduced hexacocene comonomer exceeds 2 mol. %, a second melting point of the crystalline ethylene can be observed [14] relating to side chains.

Long chain branched polypropylenes show better processing by a melt solidification compared to short chain branched polypropylenes. This is an advantage in the production of blow films and coatings. The long-chain branches have a great influence on the entangle-

ment, on the melt- and structure-viscosity as well as on the strain solidification. Metallocene catalysts are excellent tools for the production of long-chain branched polyolefins because they generate vinyl terminated oligomers by β -hydrid or β -methyl elimination which can be used for copolymerization with propene. It is possible to reach 0.1 to 1 branches per 1000 carbon atoms in the backbone chain.

EXPERIMENTAL

Materials

The white solid complex $[\text{Me}_2\text{C}(\text{Cp})_2]\text{ZrCl}_2$ and the red zirconocene complexes $[\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})]\text{ZrCl}_2$ and $[\text{Me}_2\text{Si}(9\text{-Flu})_2]\text{ZrCl}_2$ (all with purity 98 %) were purchased from MCAT-Konstanz, Germany. The yellow complex $\text{rac-}[\text{Me}_2\text{Si}(2\text{-Me-4-(1-Naph)}]\text{Ind}_2\text{ZrCl}_2$ of purity of 99 % was received from Boulder Scientific, USA.

All procedures were performed in an argon atmosphere using Schlenk techniques. Argon was purchased from Linde and purified by passing through a Messer Griesheim Oxisorb cartridge.

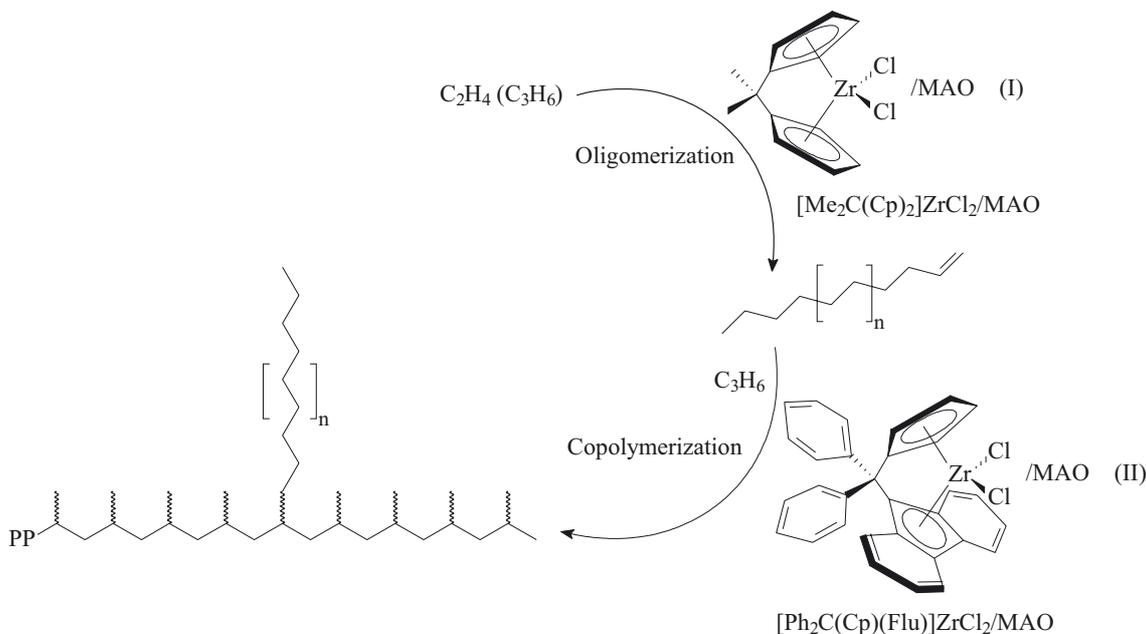
Methylalumoxane (MAO) (10 wt. % toluene solution) was purchased from Crompton. After filtration of the MAO solution, the powdered product was obtained by toluene and trimethylamine (TMA) distilling off under vacuum. The cocatalyst solution for polymerizations was prepared in dry toluene. Propene (Messer Griesheim) and toluene (Merck) were purified by passing through columns with copper catalyst (BASF R3-11) and molecular sieve 3 Å.

Synthesis of polymer

The polymerizations were carried out according to Scheme A in a 1 dm³ Büchi glass reactor equipped with a magnetic stirrer. For cleaning, the reactor was evacuated at 90 °C for 1 hour, rinsed several times with argon and cooled down to 60 °C. In a first step, ethylene monomer was produced by filling the reactor with 400 cm³ of toluene and 400 mg of MAO. The ethylene pressure was adjusted to the desired concentration of ethylene. After the saturation, polymerization was started by injection of the metallocene 1 [formula (I) in Scheme A] solution. The oligomerization was controlled by a Brooks Mass Flow Controller and the consumption

of 5.1 g of ethylene (4.5 dm³ under normal pressure). Not reacted ethylene was blown up, the suspension washed with argon to remove the last parts of ethylene and then filled with propene. The first metallocene 1 under the chosen conditions is not able to cause propene polymerization and therefore could remain in the solution. After saturation the copolymerization of ethylene macromonomers and propene was started by injection of metallocene 2 [for example (II) in Scheme A] solution. The

Gel permeation chromatography (GPC) measurements were carried out using a Waters GPC 2000 Alliance system equipped with a refractive index detector, viscosimetric detector and three columns of Styragel type. The particle size for each column was 100 μm, and the pore sizes were 10³ (HT3), 10⁴ (HT4), and 10⁶ Å (HT6). 1,2,4-Trichlorobenzene was used as the solvent. The experiments were performed at temp. 140 °C using flow rate of 1.0 cm³/min. The columns



Scheme A. Scheme of the direct copolymerization of propene with long-chain α -olefin

polymerization was quenched after 30–180 min by injection of 1 cm³ of ethanol. The polymer solution was stirred overnight in an ethanol/HCl aqueous solution, filtered and washed with ethanol.

The copolymer was extracted from the ethylene macromonomers by a method of Kong *et al.* [15]. The stabilized copolymer was extracted with *p*-xylene in a refluxing equipment at temp. 120–130 °C and quenched by dropwise added ethylene glycol monomethylester. After some cycles, most of the macromonomer was removed with the solution. The separated copolymer was dried in vacuum at temp. 60 °C overnight.

Methods of testing

¹³C NMR spectra were recorded using a Bruker Ultrashield 400 spectrometer. Samples were tested at temp. 100 °C and frequency 100.62 MHz. Samples were prepared by dissolution of 200–300 mg of polymers in 2.5 cm³ of hexachloro-1,3-butadiene and 0.5 cm³ of 1,1,2,2-tetrachloroethane-d₂.

DSC curves were recorded using a Mettler Toledo DSC 821^c instrument calibrated with *n*-heptane, mercury, gallium, indium, and zinc. Results of the second thermal cycle are presented exclusively.

were calibrated with polystyrene standards of a narrow molar mass distribution. The sample concentration was 1 mg/cm³ and the injection volume was 0.215 cm³. 2,6-Di-*tert*-butyl-4-methylphenol was used as a thermal stabilizer.

RESULTS AND DISCUSSION

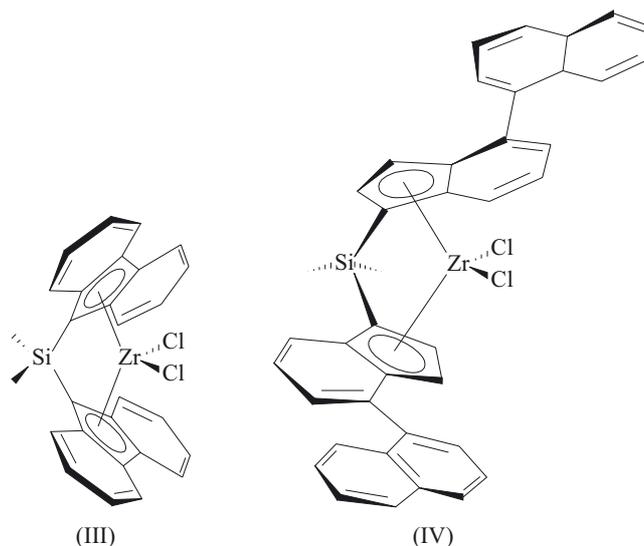
New long-chain branched polypropylenes were synthesized with oligoethylene side chains. In a first step, ethylene macromonomers were produced with a suitable metallocene 1 catalyst and then in a second step they copolymerized with propene and an additional metallocene 2 in a one pot reaction (Scheme A).

Table 1. Polymerization conditions and properties of selected ethylene macromonomers prepared using metallocene 1 catalyst—[Me₂C(Cp)₂]ZrCl₂

Polymerization temp., °C	Average C-number	M _w g/mol	T _m , °C	M _w /M _n	Content of vinyl end-groups, %
30	214	11 846	107.9	2.2	88
60	428	6380	107.2	2.6	98
90	828	3250	104.9	2.4	98

Three different macromonomers were produced by changing the temperature of first step of reaction according to Table 1. After the consumption of 5.1 g of ethylene (5 g of macromonomer production) the reaction was stopped by removal of the residual ethylene. The macromonomers were not isolated to avoid reactions of the vinyl terminated end groups. After saturation of the solution with propene, metallocene 2 was added to start the copolymerization. To obtain syndiotactic, atactic or isotactic backbones, the different types of metallocene 2 were used. C_5 -symmetric catalyst $[\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})]\text{ZrCl}_2/\text{MAO}$ [formula (II) in Scheme A] produces syndiotactic polypropylene (sPP), C_1 -symmetric catalyst $[\text{Me}_2\text{Si}(9\text{-Flu})_2]\text{ZrCl}_2/\text{MAO}$ [formula (III)] produces atactic polypropylene (aPP) and C_2 -symmetric catalyst $\text{rac}[\text{Me}_2\text{Si}(2\text{-Me-4-(1-Naph)-1-Ind)}_2]\text{ZrCl}_2/\text{MAO}$ [formula (IV)] produces isotactic polypropylene (iPP).

The separation of the unreacted macromonomer from the copolymer was difficult. Up to 4 extraction steps were necessary. The yields of the cleaned copolymers were 20 up to 60 %. Figure 1 shows GPC curves of samples prepared with use of three different zirconocene catalysts [formula (II)—(IV)] and after one, two, or three extraction steps. The macromonomer has molar mass equal 3000 g/mol.



The GPC curves of the polymer mixtures without extraction step are always bimodal. It is most easy to clean the copolymer with the isotactic backbone (Fig. 1c). Here only one extraction step is necessary because the copolymer is much more insoluble than the macromonomer. Most extraction steps are needed for copolymer with a syndiotactic backbone (Fig. 1a). The molar masses and microstructures of cleaned copolymers were investigated (Table 2).

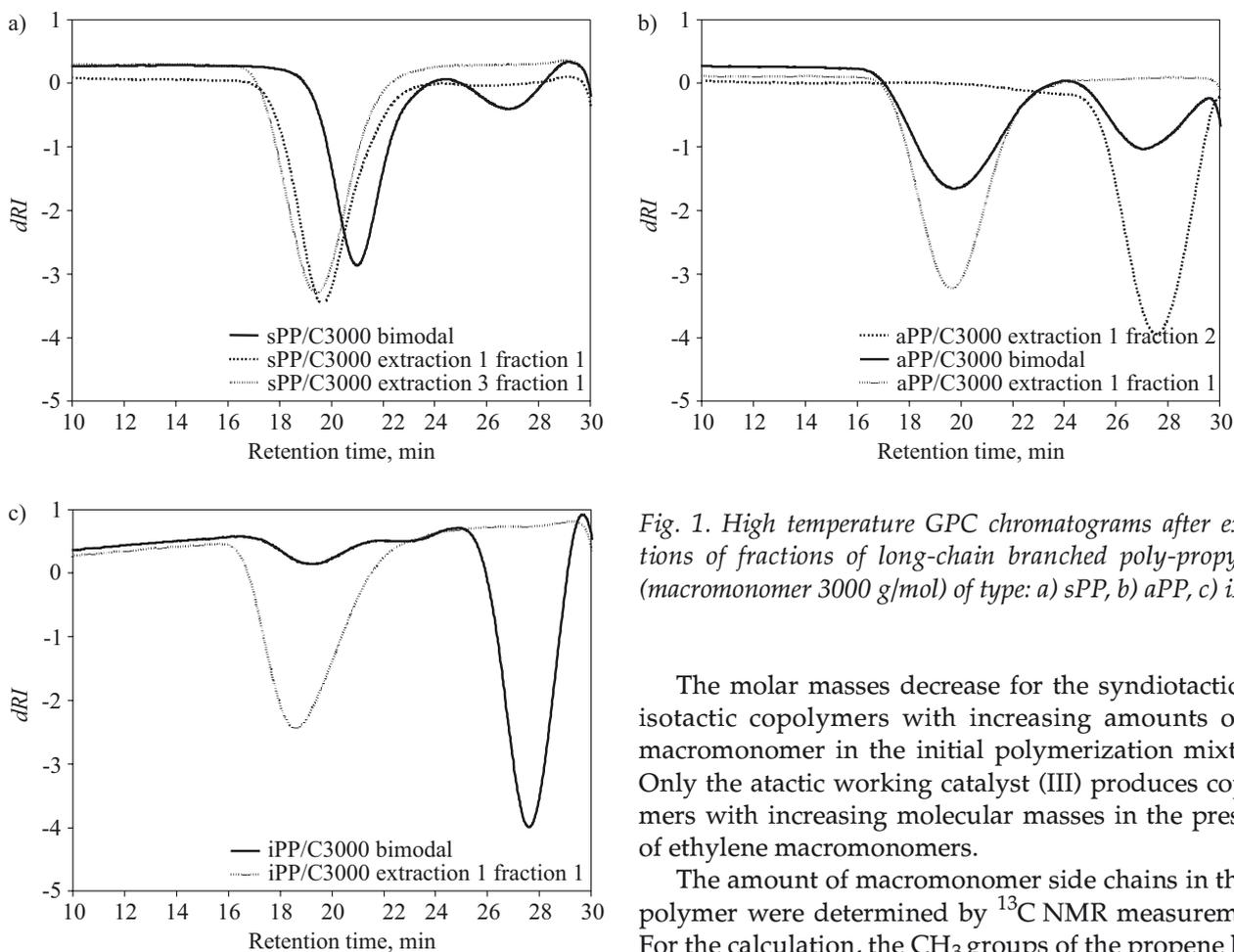


Fig. 1. High temperature GPC chromatograms after extractions of fractions of long-chain branched poly-propylenes (macromonomer 3000 g/mol) of type: a) sPP, b) aPP, c) iPP

The molar masses decrease for the syndiotactic and isotactic copolymers with increasing amounts of the macromonomer in the initial polymerization mixtures. Only the atactic working catalyst (III) produces copolymers with increasing molecular masses in the presence of ethylene macromonomers.

The amount of macromonomer side chains in the copolymer were determined by ^{13}C NMR measurements. For the calculation, the CH_3 groups of the propene back-

Table 2. Effect of the macromonomer concentration in the reaction mixture on molar masses of copolymers; propene concentration 1 mol/dm³, polymerization temperature 45 °C

Type of catalyst	M_w of macromonomer g/mol	Content of macromonomer in the reaction mixture, mol. %	M_w of copolymer g/mol	Macromonomer in copolymer mol. %	Macromonomer in copolymer wt. %	rr-triads content, %
syndiotactic working [formula (II)]	—	0	386 000	0	0	0.09
	11 600	0.043	376 000	0.0022	0.59	0.09
	6500	0.077	256 000	0.012	1.75	0.09
	3000	0.17	178 000	0.037	2.57	0.08
atactic working [formula (III)]	—	0	157 000	0	0	16
	11 600	0.043	328 000	0.0004	0.12	18.2
	6500	0.077	294 000	0.0021	0.20	16.4
	3000	0.17	360 000	0.003	0.45	18.0
isotactic working [formula (IV)]	—	0	650 000	0	0	99.9
	11 600	0.043	653 000	0.0012	0.32	97.9
	6500	0.077	625 000	0.0038	0.57	97.6
	3000	0.17	587 000	0.013	0.89	97.0

bone units (20.19 ppm sPP; 20.76 ppm, aPP; 21.91 ppm, iPP) and the CH₂ groups of ethylene macromonomer units (29.92 ppm) were used. As expected, the amount of macromonomer units in the copolymer increases with the macromonomer concentration in the initial phase and with decreasing chain length. 2.50 wt. % of macromonomer units in the copolymer could be obtained. This means that there are in average 1.5 branches per polymer chain for molar mass of 180 000 g/mol. For most other samples in Table 2, the number of branches is less than 1.

The atactic working catalyst (III) incorporates the lowest number of macromonomers while the syndiotactic working catalyst (II) the highest number of them. The catalyst (II) has the most open structure and therefore can incorporate easier bulky macromonomers. Catalyst (IV) is more sterically hindered by the naphthyl substitution of the indenyl ligands.

For all copolymerization reactions, the influence of the comonomer concentration on the tacticity is low. The concentration of the measured meso diads is nearly constant over the whole varied concentrations of the macromonomer and also does not depend on the macromonomer chain length. Only for the syndiotactic working catalyst (II), the tacticity is lower (89 %) for the highest macromonomer concentration. Different is an influence of amount of macromonomer in the copolymer on the melting temperatures (T_m) of the copolymers.

As it can be seen in Figure 2 increasing amounts of macromonomer cause a significant decrease in T_m . For the isotactic backbone, the melting point decreases from 160 °C (0 % incorporation of macromonomer) to 140 °C (0.013 mol. % incorporation) and for the syndiotactic PP from 127 °C (0 % incorporation) to 112 °C (0.037 mol. % incorporation). This shows that already few side chains of the long-chain macromonomer can strongly decrease melting point of iso- or syndiotactic polypropylene.

The incorporation of macromonomers can be increased if the propene pressure is decreased. For these

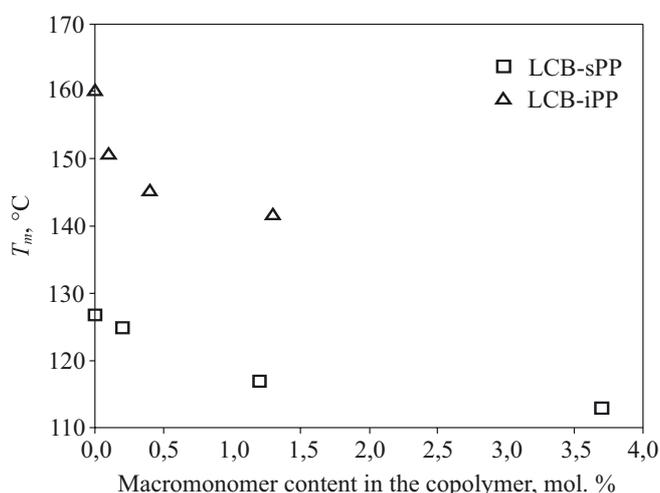


Fig. 2. Influence of molar fraction of macromonomer in the copolymer on melting temperature (T_m) of the long chain branched iso- and syndiotactic polypropylenes (LCB-iPP and LCB-sPP)

experiments only catalyst (II) was used because it showed the highest possibility of incorporation of macromonomers. The results are presented in Table 3.

The macromonomer (3000 g/mol) concentration in the copolymer increases to 0.30 mol. % or 17 wt. %, if the propene concentration is only 0.1 mol/dm³. From similar molar mass of 180 000 g/mol it can be calculated that in average the polypropylene backbone chain has 8 macromonomer side chains. For the other macromonomers it was also found that more of them is inserted if the propene concentration is smaller. The last copolymer in Table 3 contains 0.135 mol. % (26 wt. %) of the long-chain macromonomer (11 600 g/mol) for propene presence in the reaction mixture of 0.1 mol/dm³.

The molar masses increase for all three macromonomers with increasing propene concentration and are higher than those obtained for the propene homopolymerization. The highest value 423 000 g/mol was

Table 3. Copolymerization of propene with different ethylene macromonomers of $M_w = 3000$ g/mol, 6500 g/mol or 11 600 g/mol at different propene concentration using the syndiotactic working catalyst [formula (II)]

Propene concentration mol/L	M_w of macromonomer g/mol	Macromonomer in reaction mixture mol. %	Macromonomer in copolymer mol. %	M_w of copolymer g/mol	T_m , °C	rr-triads content %
0.5	—	0	0	232 000	123.2	90.9
0.2	—	0	0	148 000	116.4	87.1
0.1	—	0	0	116 000	107.6	85.1
0.5	3 000	0.17	0.10	394 000	105.7	87.6
0.2	3 000	0.17	0.25	245 000	89.2	86.3
0.1	3 000	0.17	0.30	180 000	86.0	85.1
0.5	6 500	0.077	0.053	403 000	112.5	89.9
0.2	6 500	0.077	0.080	235 000	105.0	85.8
0.1	6 500	0.077	0.112	165 000	98.0	80.9
0.5	11 600	0.043	0.033	423 000	120.0	88.0
0.2	11 600	0.043	0.078	210 000	108.1	86.7
0.1	11 600	0.043	0.135	150 000	100.5	85.1

reached for a copolymer with a macromonomer mass of 11 600 g/mol and for propene presence of 0.5 mol/dm³ while that was only 232 000 for homopolymerization in the same conditions. The chain length of the macromonomer has only a weak influence on the copolymer molar mass. Such effect was observed in the past mainly for the polymerization activities [16–18]. If the activity is increased by the comonomer and the transfer reaction stays constant, the molar mass of the copolymer will increase.

The tacticity is not much influenced by the macromonomers (see Tab. 3, rr-triads content). Only for the highest propene concentration the homopolypropylene (rr-triads content is 90.9 %) shows higher syndiotacticity than copolymers (rr-triads content in the range 87.6–89.9). rr-Triads contents of 85 % were found as well for the copolymers with the different macromonomers as for the homopolymer obtained using propene concentration of 0.1 mol/dm³.

A significant influence can be observed on T_m values of the copolymers. As expected for all copolymers, T_m values are lower than for the homopolymer. The concentration of 0.14 mol. % of the macromonomers (6500 and 11 600 g/mol) is sufficient to decrease T_m of the syndiotactic polypropylene by 25 deg to about 100 °C. For the macromonomer with a molar mass of 3000 g/mol, 0.25 mol. % incorporation to copolymer is necessary to give the same effect.

CONCLUSIONS

It could be shown that it is possible to synthesize long-chain branched polypropylenes with use of metallocene catalysts. Ethylene based macromonomers of molar masses of 3000, 6500 or 11 600 g/mol could be synthesized and copolymerized with propene in a one pot reac-

tion with use of different zirconocene/MAO catalysts. Most efficient for the long-chain macromonomers is a syndiotactic working metallocene [C_s -symmetric, formula (II)] while the atactic working catalyst [formula (III)] gives the lowest incorporation. With the C_s -symmetric catalyst, the relationship of branch content and branch length was investigated to determine some material performances. The maximum comonomer content of 0.30 mol. % in the polymer was reached with the shortest macromonomer at a propene concentration of 0.1 mol/dm³. Copolymers with the longest macromonomers reach a maximum of 26 wt. % of macromonomer content in the copolymer.

A decreasing stereoregularity with increasing macromonomer content in the polymer can be observed, too. This effect depends on the population of branches but also on the side chain length. With increasing side chain length, the tacticity decreases much more intensively. The investigation of the thermal behavior shows a decrease in T_m with increasing population of branches, but variation of the side chain length has no effect.

New kinds of polypropylene materials can be obtained by this one pot copolymerization.

REFERENCES

- Galli P., Vecellio G.: *J. Polym. Sci. A* 2004, **42**, 396.
- Razavi A., Thewalt U.: *Coordination Chem. Reviews* 2006, **250**, 155.
- Angermund K., Fink G., Jensen V. R., Kleinschmidt R.: *Chem. Rev.* 2000, **100**, 1457.
- Kaminsky W.: *Catal. Today* 2000, **62**, 23.
- Kaminsky W.: *J. Chem. Soc. Dalton Trans.* 1998, 1413.
- Coates G. W.: *Chem. Rev.* 2000, **100**, 1233.
- Piel C., Stadler F. J., Kaschta J., Rulhoff S., Münstedt H., Kaminsky W.: *Macromol. Chem. Phys.* 2006, **207**, 26.
- Boger A., Heise B., Troll C., Marti O., Rieger B.: *Europ. Polym. J.* 2007, **43**, 634.
- Rulhoff S., Kaminsky W.: *Macromol. Symp.* 2006, **236**, 161.
- Stern C., Frick A. R., Pater J. T. M., Weickert G.: *Macromol. Mater. Eng.* 2005, **290**, 372.
- Poon B., Rogunova M., Hiltner A., Baer E., Chum S. P., Galeski A., Piorkowska E.: *Macromolecules* 2005, **38**, 1232.
- Arnold M., Henschke O., Knorr J.: *Macromol. Chem. Phys.* 1996, **197**, 563.
- Quijada R., Guevara J. L., Galland G. B., Rabagliati F. M., Lopez-Majada J. M.: *Polymer* 2005, **46**, 1567.
- Rulhoff S., Kaminsky W.: *Macromol. Chem. Phys.* 2006, **207**, 1450.
- Kong J., Fan X., Jia M.: *J. Appl. Polym. Sci.* 2004, **93**, 2542.
- Kaminsky W.: *J. Polym. Sci., Part A: Polym. Chem.* 2004, **42**, 3911.
- Quijada R., Dupont J., Miranda M. S. L., Scipioni R. B., Galland G. B.: *Macromol. Chem. Phys.* 1995, **196**, 3991.
- Chien J. C. W., Nozaki T.: *J. Polym. Sci., Part A: Polym. Chem.* 1993, **31**, 227.