Russian Chemical Reviews **71** (1) 49 – 70 (2002) © 2002 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2002v07n01ABEN00698

Controlled synthesis of stereoblock polypropylene. New trends in the development of elastomers

N M Bravaya, P M Nedorezova, V I Tsvetkova

Contents

I. Introduction 49
II. Catalyst systems for the synthesis of elastomeric stereoblock polypropylene 50
III. Characteristic features of the structure of elastomeric stereoblock polypropylene and the nature of relaxation processes 65
IV. Conclusion 67

Abstract. The review generalises published data on the synthesis of elastomeric stereoblock polypropylene, a representative of thermoelastoplastics, which are prepared by random or block copolymerisation of various co-monomers and are widely used in the manufacture of diverse mechanical rubber goods. New unique applications of metallocene and post-metallocene catalysts in the design of polyolefin elastomers with a broad spectrum of physicomechanical characteristics are discussed. Particular attention is given to modern homogeneous catalyst systems based on Group IVB element metallocene complexes, which ensure highly efficient synthesis of polypropylene elastomers with various stereoblock structures. Data on the specific features of the structure and properties of the elastomeric stereoblock polypropylene are analysed. The bibliography includes 160 references.

I. Introduction

Homo- and copolymers of α-olefins currently rank as one of the most important industrial polymeric materials. The world manufacture of polyolefins such as high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), and isotactic polypropylene (IPP), estimated as tens million tons a year, constantly increases and now it accounts for more than 50% of the output of all manufactured plastics.[1] Expansion of the production of these materials was promoted by the discovery of metal complex Ziegler – Natta catalysts with high activity and regio- and stereospecificity.[2–4] At present, industrial processes, mainly, the synthesis of IPP, make use of fourth-generation heterogeneous Ziegler – Natta catalysts containing $TiCl_4$, δ-$MgCl_2$, Et_3Al, and modifying additives.[5–7] Due to replication (the reproduction of the shape of a catalyst particle by the growing polymer particle), the catalysts used ensure the formation of spherical polymer particles with specified size and porosity.

The range and the fields of application of homo- and copolymers of α-olefins are constantly extending. The consumption of binary ethylene – propylene and ternary ethylene – propylene – diene copolymers permanently increases.[1,8,9] The production volume of these materials exceeds a million tons a year. The industrial synthesis is performed most often using vanadium metal complex systems.[10,11] Highly effective two-stage processes for the production of heterophase copolymers based on IPP (1st stage) and ethylene – propylene copolymers (2nd stage) [1] are widely used in industry. By controlling the fraction and the composition of the copolymer and the molecular masses of polypropylene (PP) and the copolymer, one can obtain materials with enhanced elasticity and impact strength, thermoplastic polyolefins (TPO) and thermoplastic elastomers (TPE).[2–6]

A special position among polyolefins is held by elastomers. They are usually prepared by statistic or block copolymerisation of various co-monomers. Elastomers are capable of being rapidly stretched and contracted; they exhibit high strength and high modulus of elasticity in the stretched state and return to the initial size as the load has been removed. The elastic properties of these materials are due to the formation of chemical or physical networks. The physical network junctions can be represented by crystalline regions joined by the transient chains of the amorphous polymer (Fig. 1). The fractions of amorphous and crystalline phase, the average size, the size distribution, the shape of crystallites, the network density, the possibility of changing the network structure under the action of load and several other factors determine the properties of elastomeric materials.

In the last two decades, the discovery of new highly effective homogeneous systems based on metallocene complexes of Group

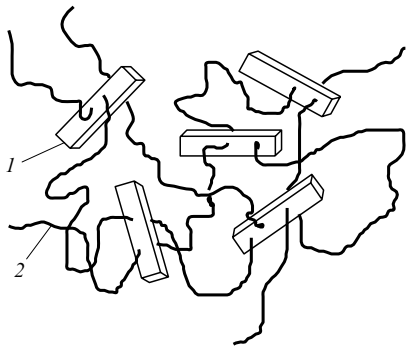


Figure 1. Schematic representation of the microstructure of elastomeric stereoblock polypropylene.
(*1*) Crystallites formed by isotactic blocks; (*2*) amorphous sections consisting of irregular blocks.

N M Bravaya Institute of Problems of Chemical Physics, Russian Academy of Sciences,142432 Chernogolovka Moscow Region, Russian Federation. Fax (7-096) 514 32 44. Tel. (7-096)522 11 31.
E-mail: nbravaya@cat.icp.ac.ru
P M Nedorezova, V I Tsvetkova N N Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, 119991 Moscow, Russian Federation. Fax (7-095) 137 82 84. Tel. (7-095) 939 73 71.
E-mail: pned@chph.ras.ru

Received 9 October 2001
Uspekhi Khimii **71** (1) 57 – 80 (2002); translated by Z P Bobkova

IVB elements activated by poly(methylaluminoxane) (MAO) or by other compounds opened up new opportunities for the development of polymer technologies and for extension of the range and applications of homo- and copolymers of α-olefins. Various aspects of metallocene and post-metallocene catalysis of olefin polymerisation have been covered in monographs, special editions and reviews.[12–20] Due to the uniformity of active centres, these catalysts make it possible to produce polymers with a narrow molecular mass distribution (MMD) and copolymers with a homogeneous composition. The narrow molecular mass distribution and structural and compositional uniformity result in enhanced mechanical strength, impact strength and clarity of materials and determine specific properties of homo- and copolymers. The successive or simultaneous conduction of polymerisation in the presence of a mixture of complexes having different structures ensures the synthesis of polymers with bi- or polymodal MMD and with a controllable composition.

When metallocene catalysts are used, the differences between the reactivities of ethylene, propylene, higher α-olefins and a number of other monomers are much less pronounced [21] than in the case of heterogeneous or vanadium systems.[22] By varying the composition, structure and the type of symmetry of metallocenes, one can control the stereospecificity of metallocene systems and prepare PP and higher poly-α-olefins with various microstructures. The use of metallocene systems not only ensures the formation of PP having different stereochemical compositions (iso-, syndio-, hemiiso- and atactic polymers) at satisfactory rates but also extends the range of applicable monomers (for example, cycloolefins and polar monomers can be involved in reactions). A large number of new materials are currently produced in industry by metallocene-catalysed processes.[23, 24]

Metallocene catalysts also open up the way for the preparation of new polymers with diverse stereo- and regiochemical structures, in particular, synthetic blends of various PP, or for the selective synthesis of stereoblock PP (SBPP). The SBPP macromolecules either consist of alternating stereoblocks with different structures or have a uniform structure separated into blocks by regularly arising 'errors'.

If the length of the co-crystallised stereoregular sequences (i) is relatively short, for example, $i \leqslant 10-12$ (Fig. 2 *a–d*), and the molecular mass of the polymer is high, the polymer exhibits elastomeric properties. The interest in the production of elastomeric stereoblock polypropylene (elSBPP) is caused by the fact that this is a way of one-pot synthesis of TPE from a single monomer, which has obvious advantages over the processes that require the use of at least two monomers. Due to the specific properties of metallocene catalyst systems and the possibilities they provide, the number of papers and patents devoted to various processes of elSBPP synthesis has substantially increased during the last five years. Quite recently, the range of PP-based elastomeric materials, presented in Fig. 2 and considered in this review, was extended by elastomeric PP (elPP), which is branched atactic PP with short regular, ordered (isotactic or syndiotactic) side chains.[25] These branches are organised in well dispersed crystalline domains connected by amorphous sections of the backbone, their presence preventing 'sliding' of the atactic chains under load, which is typical of atactic PP. Investigations by a number of companies aimed at the development of elSBPP-based materials which could replace plasticised PVC, and some other expensive elastomers are in progress, and this is largely related to the possibility of designing macromolecules in the presence of metallocene catalyst systems.[25, 26]

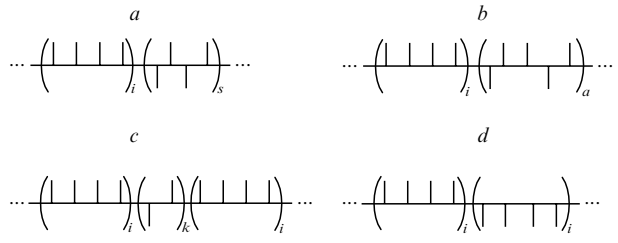


Figure 2. Schematic views of various types of SBPP.
(*a*) Alternation of isotactic and syndiotactic blocks; (*b*) alternation of isotactic and atactic blocks; (*c*) isotactic blocks with a correcting 'error'; (*d*) isotactic blocks with an extending 'error'.

The present review surveys data on the influence of the structure of catalysts and conditions of synthesis of polypropylene on the activity of catalyst systems and the structure of elSBPP; the relationship between the structure and properties (strain, relaxation, thermal, *etc.*) of the SBPP produced. The attention is focused on the homogeneous catalyst systems based on metallocene complexes of Group IVB elements.

II. Catalyst systems for the synthesis of elastomeric stereoblock polypropylene

This section considers views on the mechanism of catalytic and stereospecific action of metal-complex catalysts and on the development of methods for the analysis of polymer microstructure and its relationship with the properties of catalysts; it describes the history of the discovery of elSBPP and the development of heterogeneous catalysts and highly effective homogeneous catalyst systems for the synthesis of elSBPP.

1. Characteristics of the mechanisms of catalytic and stereospecific action of metal complex catalysts

Elucidation of the mechanisms of catalytic and stereocontrolling action of catalysts is very significant for the target-directed and controlled synthesis of polyolefins. Research into the mechanism of action of Ziegler–Natta metal complex catalysts of polymerisation is the subject of a number of monographs and reviews.[12, 13–17, 20, 27]

The currently accepted mechanism of formation of an active centre (AC) based on Shilov's and Dyachkovskii's concept [28] includes the steps of coordination of catalyst components, alkylation and ionisation of a transition metal compound to give a coordinatively unsaturated cation containing an active metal–carbon bond. These views have been further developed after the discovery of highly effective homogeneous catalyst systems based on metallocenes in combination with MAO or weakly coordinating anions such as $B^-(C_6F_5)_4$.[13–20, 24] The mechanism of action of the specific activating agents for metallocene systems is extensively studied.

Several alternative mechanisms of chain growth are described in the literature, namely, the coordinate-anionic mechanism, direct insertion of the monomer into the active metal–carbon bond and migration mechanism. On the basis of the results of recent investigations into propylene polymerisation catalysed by homogeneous syndio- and hemiisospecific metallocene catalysts, preference is given to the migration mechanism. According to this mechanism, growth of the polymer chain occurs through its migration to the coordinated monomer and insertion of the monomer. The next monomer molecule is coordinated to the newly appeared vacancy, and migration of the polymer chain and insertion are repeated; thus, after each monomer insertion event, the growing polymer chain and the coordination vacancy exchange places (the Cossee mechanism). This mechanism also assumes the possibility of chain migration to the initial position without monomer insertion with retention of the AC geometry (the Cossee–Arlman mechanism). The symmetry of the AC and the ratio between the rates of the 'monomer insertion–chain migration' and 'chain migration without monomer insertion' processes largely determine the polymer microstructure.

In terms of the two-step mechanism of chain growth, the stereocontrol can take place both at the coordination step and during monomer insertion into the metal–carbon active bond.[29–33] The insertion of the first monomer is usually not

stereospecific.[31] Stereocontrol is enhanced as a result of cooperative action of the AC, the ligand and the growing polymer chain. The views on the mechanism of stereocontrol by metal complex heterogeneous catalysts is based on the detailed investigation of the polymer microstructure and the properties of separate polymer fractions.

In conformity with the Bovey statistics,[34, 35] a polymer chain is regarded as a sequence of isotactic dyads characterised by identical arrangements of methyl groups relative to the plane of the carbon chain of the macromolecule (*m*-dyads) and syndiotactic dyads in which the methyl groups of propylene are located on different sides of this plane (*r*-dyads). Methods for determination of the contents of *m*- and *r*-dyads, triads (*mm*, *rr*, *mr*), tetrads (*mmm*, *rrr*, *mmr*, *rrm*), various pentads (iso — *mmmm*; syndio — *rrrr*, and hetero — *rmmr*, *mmrr*, *mrrr*, *rmrr*, *rrmr*, *mrmm*, *mrrm*, *mmrm*) and higher sequences (hexads, heptads, *etc*.) based on the use of high-resolution ^{13}C NMR spectroscopy have been developed.[12, 13, 17, 29, 33, 36–38]

Analysis of the configuration statistics allows one to identify the stereocontrol mechanism. Two key mechanisms are possible according to which stereocontrol is determined either by the chirality of the catalytic site or by the last inserted monomeric unit in the growing polymer chain. Correspondingly, two simple statistical models have been developed to interpret the distribution of the stereosequences in the polymer, known as the enantiomorphic model and the Bernoullian model. According to the enantiomorphic model, high stereospecificity is attained when an accidental 'error' arising during the polymer chain growth is corrected in the next step. The following ratios hold in this case: $rr:mr = 1:2$ or $mmmr:mmrr:mrrm = 2:2:1$. When the stereocontrol is accomplished by the last incorporated unit of the polymer chain, $4[mm][rr][mr]^{-2} = 1$.[37]

Methods for estimating the length of continuous isotactic sequences and the regiospecificity of catalyst systems have been developed. The degree of regiospecificity is normally determined from the ^{13}C NMR spectra of polymer solutions by analysing the proportion of abnormal patterns of monomer addition (2,1- or 1,3- instead of the 1,2-addition). Depending on the type of system and polymerisation conditions, the frequency of abnormal addition patterns can vary from fractions of a percent to tens of percent.[29, 33]

The fraction of isotactic sequences with different numbers of monomer units and the pentad composition of the polymer can vary over a broad range, depending on the stereocontrol capacity of catalyst systems, while in the case of stereoblock polymers, it is determined by the content of monomer units in regular and atactic sequences. The formation of stereoblock fractions with the use of heterogeneous catalyst systems is usually explained by the presence of highly coordinatively unsaturated AC the structure of which changes repeatedly over the period of polymer chain growth, for example, due to different ways of coordination of the cocatalyst and modifying additives. The microstructure of these materials is described using parametric models, in particular, the enantiomorphic model, the Bernoullian statistic model and the first- and second-order Markov chains.

In analysis of the mechanism of the stereocontrolling action of catalyst systems, the method of polymer fractionation by extraction with solvents having increasing boiling points is often used. The fractionation at rather high molecular masses ($> 50\,000$ g mol^{-1}) is mainly determined by the stereoregular structure of polymer chains, while at lower molecular masses, it is determined simultaneously by the molecular mass and the microstructure.[39]

When polymerisation takes place under the action of modern highly active titanium magnesium catalysts (TMC), the content of irregular fractions in the product reaches $\sim 50\%$. However, the introduction of electron-donating modifiers, for example, dibutyl phthalate as an internal donor or various dialkoxysilanes as external donors, markedly increases the isospecificity of the systems. High isospecificity of TMC is also attained by using 2,2-substituted dialkoxypropanes as modifying additives.[6] The isotactic fractions of polymers obtained with these catalysts are characterised by high contents of *mmmm* pentads ($\geqslant 94\% - 98\%$).

The discovery of highly effective stereospecific homogeneous catalysts made it possible to establish the relationship between the metallocene structure, the nature of the ligands, the type of symmetry, the mechanism of polymerisation and the microstructure of the resulting PP.[37, 40, 41] An advantage of homogeneous metal complex systems is the possibility of direct investigation of the AC nature by various physical methods. Ewen [42] has formulated the symmetry rule which establishes the relationship between the structure of the initial catalyst and the microstructure of PP synthesised using this catalyst. Thus *ansa*-metallocenes of C_2 symmetry can ensure the synthesis of IPP with a content of *mmmm* pentads of up to 99%, those of C_s symmetry provide the synthesis of syndiotactic PP with up to 94% of *rrrr*-pentads, C_{2v} symmetry leads to atactic PP, and C_1 symmetry provides hemiisotactic, isotactic or stereoblock PP depending on the type of π-bonded ligands and substituents in them. Catalysts with C_2 symmetry are characterised by homotopic, C_s, by enantiotopic, and C_1, by diastereotopic coordination positions of the olefin and the growing polymer chain. The knowledge of the mechanistic details of the stereo- and regiocontrol of the polymer gives a key to the rational design of homogeneous catalysts. By changing the metallocene structure, the type of symmetry, the ligands and substituents in the ligands and in bridges and by varying the conditions of polymerisation, one can control the microstructure, the molecular mass, and the terminal groups of polymers in the desired direction and produce materials with necessary properties. In the case of metallocene catalysts, unlike heterogeneous catalyst systems, polymerisation conditions (reaction temperature and monomer concentration) influence appreciably the stereo and regio structure of the resulting polymers.

2. Heterogeneous Ziegler–Natta catalyst systems for selective synthesis of elastomeric stereoblock polypropylene

It was found in the first of Natta's studies that PP formed in the presence of isospecific catalyst systems based on the layered violet modifications of α- or δ-$TiCl_3$ and Et_3Al (or Et_2AlCl) as a cocatalyst contains ~ 80 mass % of the major substance, isotactic crystalline PP insoluble in boiling n-heptane,[43, 44] $\sim 5\%$ of amorphous low-molecular-mass atactic PP soluble in ether, and $\sim 15\%$ of an intermediate fraction soluble in boiling n-heptane. It was shown that fractions with degrees of crystallinity of 15%–30% and an intrinsic viscosity of ~ 1 dl g^{-1}, unlike isotactic fractions, exhibit 'stress–strain' curves typical of elastomers, namely, a low initial modulus of elasticity, its substantial decrease upon stretching to 200%–300% and an increase in the modulus and strength upon further stretching (Fig. 3). A number of other properties typical of elastomers have been noted. A stereoblock structure has been proposed for this polymer.[43, 44]

In 1982, the synthesis of high-molecular-mass elSBPP induced by tetraalkyl or tetraaryl derivatives of titanium, zirconium and

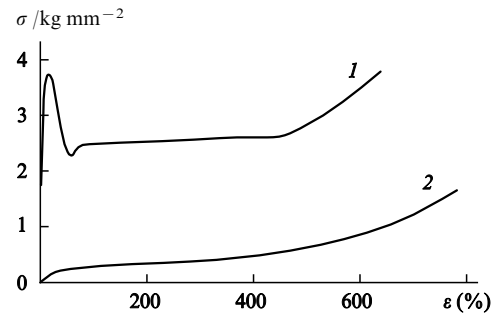


Figure 3. Stress (σ)–strain (ε) curves for highly isotactic (*1*) and stereoblock (*2*) fractions of PP.[43]

Table 1. Polymerisation of propylene catalysed by Collette catalyst systems (liquid propylene, 50 °C, 1 h).[45–47]

Row	Catalyst	[Cat.] (see [a])	A (see [b])	$10^{-3}M_\eta$ (see [c])	D_{993}/D_{975} (see [d])	T_m /°C (see [e])	C (%) (see [f])	F_{Et_2O} (%) (see [g])
1	$ZrBn_4$	0.3	0.08	2450	0.40	148	7	–
2	$ZrBn_4$ (see [h])	0.4	0.17	520	0.53	155	23	41
3	$Zr(C_5H_5CMe_2)_4$	0.5	0.15	1430	0.57	153	27	–
4	$Zr(C_5H_5CMe_2)_4$ (see [h])	0.2	0.53	376	0.46	149	11	54
5	$Zr(C_5H_5CMe_2)_4$ (see [h])	0.6	0.12	456	0.55	155	24	42
6	$Zr(C_5H_5CMe_2)_4$ (see [h, i])	0.2	0.59	395	0.56	156	27	–
7	$Zr(Bu^tCH_2)_4$	0.2	0.23	2737	0.30	144	9	–
8	$Zr(Bu^tCH_2)_4$	0.6	0.12	2016	0.52	153	20	–
9	$TiBn_4$ (see [h])	0.2	0.18	1163	0.53	150	29	37
10	$TiBn_4$ (see [j])	0.2	0.29	1287	0.56	153	20	–

[a] Catalyst loading expressed in mmol (g Al_2O_3)$^{-1}$. [b] Catalyst activity expressed in kg of PP (mmol M)$^{-1}$ h^{-1}, where M is a transition metal. [c] Viscosity-average molecular mass (in g mol^{-1}) calculated from the intrinsic viscosities (taken from Ref. 46) using the Mark–Houwink equation with the parameters $K = 1.58 \times 10^{-4}$, $\alpha = 0.77$. [d] Macrotacticity index of polymer samples determined from the intensities of the absorption bands at 993 and 975 cm^{-1} in the IR spectra. [e] Melting temperature. [f] Degree of crystallinity calculated from the heats of melting (taken from Ref. 46): $C = (\Delta H_m/209) \times 100$, where ΔH_m is the heats of melting (in J g^{-1}), 209 J g^{-1} is the specific heat of melting of crystalline polypropylene. [g] Content of the fraction soluble in diethyl ether. [h] During polymerisation, hydrogen was introduced (~3 atm). [i] Polymerisation was carried out with the addition of triisobutylaluminium (TIBA), Al : Zr = 1. [j] The catalyst was preliminarily hydrogenated for 20 min at 25 °C.

hafnium immobilised on Al_2O_3 [with a specific surface area (S_{sp}) of 100–150 m^2 g^{-1}] has been patented.[45] These catalyst systems allow the preparation of high-molecular-mass PP (with an intrinsic viscosity of 1.5–13.0 dl g^{-1}) with low or moderate degrees of crystallinity (5%–30%) and high melting points (135–155 °C).[46,47] The glass transition temperature (T_g) of the polymers varies from −7 to −10 °C. The content of fractions soluble in ether and heptane ranges from 30% to 50%, depending on the catalyst and polymerisation conditions. The polydispersity coefficients of the polymer samples also vary over wide limits, $M_w : M_n = 6–23$ (M_w and M_n are the weight average and number average molecular masses of the polymer, respectively).

The influence of the nature of the transition metal, the ligands attached to it and polymerisation conditions on the activity and properties of the resulting polymer is illustrated by the data of Table 1.[45–47] Zirconium complexes with bulky ligands (neopentyl or neophyl) lead to the formation of PP with a higher degree of isotacticity than $ZrBn_4$ (see Table 1, rows 8, 3, 1). The stereospecificity of tetraneophyl and tetraneopentyl complexes of zirconium depends appreciably on the concentration of the supported catalyst. An increase in the content of the complex on the support (correspondingly, an increase in the Zr : Al ratio) is accompanied by an increase in the isotacticity of the resulting polymer and simultaneous decrease in the catalyst activity (see, for example, rows 4, 5 and 7, 8).

When the zirconium complex is pre-hydrogenated, or polymerisation is conducted in the presence of hydrogen (to control the molecular mass of polymers), the catalyst activity substantially increases and the crystallinity of the resulting polymer decreases due to the increase in the content of the elastomer fraction. It should be noted that upon the addition of stoichiometric amounts of triisobutylaluminium or diisobutylaluminium hydride, the crystallinity of polymers markedly increases (see Table 1, rows 6, 4). Titanium complexes are more active than zirconium complexes. In the presence of hydrogen, the activity of titanium complexes decreases by about 20% and becomes comparable with the activity of zirconium complexes under similar conditions. The molecular mass of PP obtained under the action of titanium complexes is much higher. The crystallinity of polymers synthesised using titanium complexes in the presence of hydrogen is relatively high (see Table 1, rows 9, 10).

To characterise the elastomeric properties of polymers, most researchers use either the recovery or the residual elongation, which are determined by the following relations

$$\frac{l_{max} - l_1}{l_{max} - l_0} \cdot 100\% \text{ or } \frac{l_1 - l_0}{l_0} \cdot 100\%,$$

where l_{max} is the maximum elongation, l_1 is the sample length after relaxation, l_0 is the length of the initial sample.

The results of mechanical tests of samples of elastomeric PP obtained in the studies by Collette are presented in Fig. 4. It can be seen that the polymers synthesised possess good elastomeric properties. Upon stretching by 300%, the residual elongation is 93%. However, it was found that mechanical compositions obtained by blending the high-molecular-mass fraction soluble in ether with the fraction insoluble in hexane exhibit similar properties (see Fig. 4, dashed lines). After blending for 10 min at 180 °C, the percentage of the ether-soluble fraction decreased from 69% to 37%.[46] It was concluded [46] that the key role is played by the high-molecular-mass atactic fraction, which can be co-crystallised with a more stereoregular fraction to give cross-linked structures, and the following criterion was introduced: a catalyst effective for the formation of elSBPP should possess relatively low

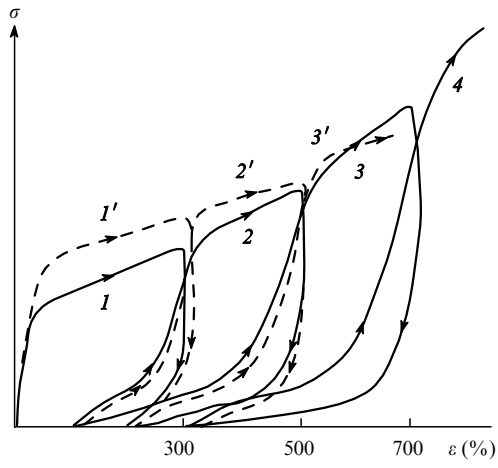


Figure 4. Hysteresis tests of elastomeric SBPP (*1*–*4*) and mechanical mixtures (*1′*–*3′*) of ether-soluble (M_η = 284000 g mol^{-1}) and hexane-insoluble (M_η = 1478000 g mol^{-1}) fractions.[46]
The rate of sample drawing and unloading is 51 cm min^{-1}.
Draw ratio (%): (*1*, *1′*) 300; (*2*, *2′*) 500; (*3*, *3′*) 700; (*4*) 820.

stereospecificity and ensure the production of a high-molecular-weight polymer.

Later, Job[48] developed modified heterogeneous titanium magnesium catalysts for the synthesis of stereoblock elPP. The catalysts were prepared by the reaction of $TiCl_4$ with $Mg(OAlk)_2$ in the presence of electron-donating substances (dialkyl phthalates) and activated by an organoaluminium compound with addition of a reagent to control stereoselectivity (heterocyclic aromatic nitrogen-containing compounds: 2,6-lutidine or pyrazine). In the absence of a nitrogen-containing modifying agent, these catalyst systems allow the synthesis of isotactic PP, while in the presence of this agent, stereoblock PP with short syndiotactic blocks is obtained. The specific activity (per g of the catalyst) of the TMC is 50–100 times as high as that of the Collette catalysts: ~9 kg PP (g Cat.)$^{-1}$ h^{-1} and ~200 g PP (g Cat.)$^{-1}$ h^{-1}, respectively. The PP samples contained ~50% of isotactic pentads, the elongation at rupture reached 1000%, and the residual elongation after stretching to 300% was ~70%–85%.

It was shown [49,50] that the use of heterogeneous vanadium systems, for example, VCl_3 together with TIBA, results in the formation of PP with an increased proportion of abnormal additions of the monomer (2,1- or 1,3- instead of the typical 1,2-addition) due to the lower stereo- and regioselectivity of vanadium systems. The resulting polymer possesses a number of properties typical of elastomeric PP, namely, low Young's modulus, the absence of yield point and high impact strength. In addition, it has a high frost resistance.

The elastomeric SBPP synthesised on heterogeneous catalyst systems has a broad MMD (Fig. 5) and can be separated into fractions by treatment with various solvents. The broadest MMD is observed for the most stereoregular fractions (see. Fig. 5). This property, common to heterogeneous catalyst systems, is a consequence of the multi-site nature of the AC formed in heterogeneous catalysts; it hampers the target-directed synthesis of polymers with specified characteristics.

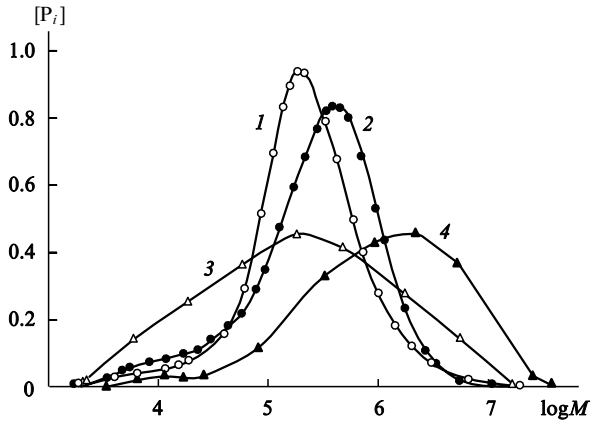


Figure 5. The molecular-mass distributions of the fractions of elSBPP prepared with the Collette catalysts (1,3,5-trichlorobenzene, 135 °C).[46] (*1*) elSBPP soluble in ether; (*2*) non-fractionated elSBPP; (*3*) elSBPP soluble in heptane; (*4*) elSBPP insoluble in hexane, [P_i] is the proportion of the polymer fraction.

3. Metallocene catalysts for the synthesis of elastomeric polypropylene

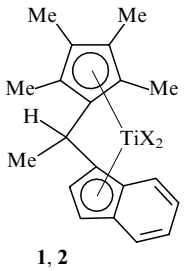
The next generation of catalysts used for the synthesis of elSBPP are homogeneous catalyst systems based on metallocene complexes of Group IVB elements activated by MAO. Advantages of these systems include high activity and the possibility of obtaining elSBPP as the only reaction product or as the predominant fraction. In addition, by selecting metallocenes and polymerisation conditions, one can control the microstructure of the growing polymer chain and change the molecular-mass characteristics of PP over wide limits.[19]

There are several types of homogeneous metallocene catalyst systems efficient in the synthesis of elSBPP, which differ in the mechanism of action. Since the AC structure, the stereocontrol mechanism and the properties of the resulting polymer are interrelated for these catalysts, it is expedient to consider various types of catalyst systems and the proposed mechanisms of polymerisation and to analyse the properties of the resulting elSBPP. It should be noted, however, that most of the mechanisms, although based on modern views and confirmed by some experimental results and model calculations, are still under discussion and require more detailed experimental evidence.

The main types of homogeneous catalyst systems for the synthesis of elSBPP include *ansa*-metallocenes with C_1 symmetry in the presence of the MAO cocatalyst; bisindenyl 2-aryl-substituted metallocenes in the presence of MAO; 'hybrid' metallocene systems in which metallocenes of several types are used simultaneously; alkylated bisindenyl 2-aryl-substituted metallocenes activated by TIBA, and post-metallocene catalyst systems.

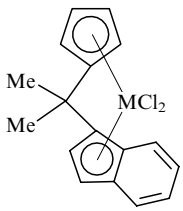
a. *ansa*-Metallocenes with C_1 symmetry activated by polymethylaluminoxane

The synthesis of elSBPP with macromolecules consisting of alternating short stereoregular crystallisable and atactic sequences catalysed by MAO-activated asymmetric titanocenes **1** and **2** was first reported by Chien and coworkers.[51–55] Under certain conditions, the reaction gave PP completely soluble in ether. For the polymer obtained at 25 °C, analysis of the density of amorphous and crystalline PP blocks[52] made it possible to estimate the lengths of atactic and isotactic blocks; they were 50 and 20 monomer units, respectively. Propylene polymerisation catalysed by a series of structurally homogeneous metallocenes **3**–**7** in the presence of the MAO cocatalyst has also been studied.[56–58] The catalytic properties of these systems, their dependence on the nature of the metallocene and on the polymerisation conditions and some characteristics of the resulting elSBPP samples are presented in Table 2.



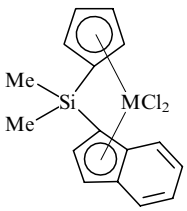
1, 2

X = Cl (**1**), Me (**2**).



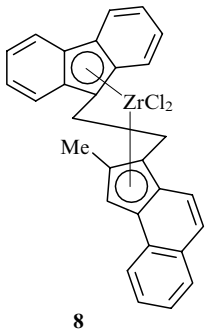
3–5

M = Ti (**3**), Zr (**4**), Hf (**5**).

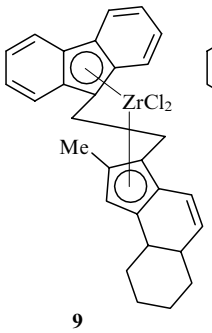


6, 7

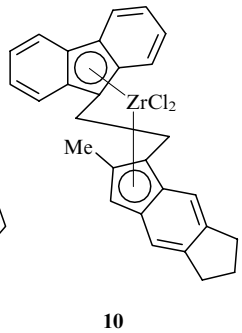
M = Zr (**6**), Hf (**7**).



8



9

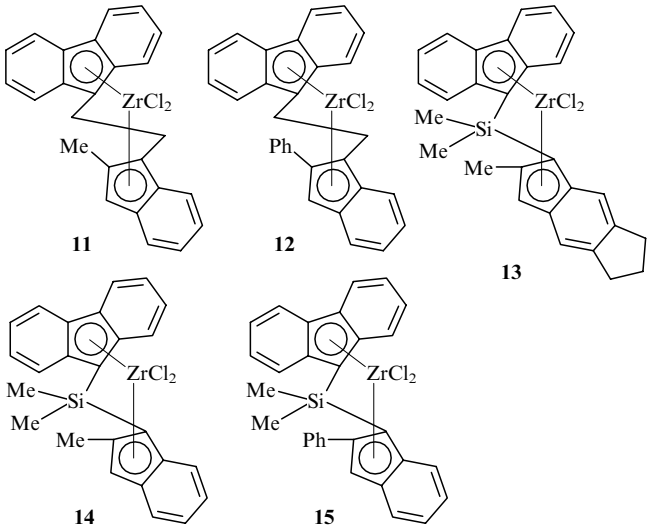


10

Table 2. Polymerisation of propylene induced by *ansa*-metallocenes with C_1 symmetry (MAO cocatalyst, Al : M = 2000).[51–53, 56–59]

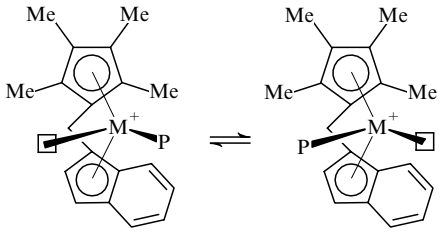
Row	Complex	$p_{C_3H_6}$ /atm	T_p /°C (see [a])	A [b]	$10^{-3} M_w$ /g mol^{-1}	$M_w : M_n$	[*mmmm*] (%) (see [c])	T_m /°C (see [d])	C (%)
1	**1**	1.0	25	–	127	3.0	40	51/66	7
2	**3**	1.0	−25	0.001	–	–	72	–	–
3	**3**	see [e]	25	0.002	70	2.3	42	–	–
4	**4**	1.0	25	1.0	22	2.0	15	–	–
5	**6**	1.0	25	1.1	9	1.8	30	–	–
6	**5**	1.0	25	1.9	30	2.1	38	47/61	–
7	**5**	3.0	25	1.6	43	2.1	32	see [f]	–
8	**5**	3.0	0	0.01	75	2.1	30	see [f]	–
9	**7**	1.0	25	2.4	49	1.7	54	54/93	19
10	**7**	4.0	25	–	140	1.9	45	50/79	15
11	**7**	3.0	0	–	380	1.9	52	53/74	17
12	**10**	2.0	30	2.0	55	1.8	43	–	–
13	**10**	6.5	30	2.3	171	2.0	37	50	–
14	**10**	7.5	50	4.6	46	1.9	49	–	–
15	**13**	2.0	30	see [g]	103	1.8	62	–	–
16	**13**	8.5	30	see [g]	158	1.9	44	–	–
17	**13**	7.5	50	see [g]	85	1.9	67	–	–

[a] Polymerisation temperature. [b] Here and in Tables. 3, 7 and 8 the activity is expressed in kg PP (mmol M)$^{-1}$ $[C_3H_6]^{-1}$ h^{-1}, where M is a transition metal. [c] Content of isotactic pentads determined from the ^{13}C NMR spectra. [d] Here and in Table 6, two T_m values are presented corresponding to two melting peaks observed in the DSC curves. [e] Polymerisation was carried out in the liquid monomer. [f] Amorphous polymer. [g] The sample is unstable.



Of the series of catalysts **1**–**7**, the hafnium complexes **5** and **7** are the most effective. They combine rather high activity and stability; they catalyse the formation of PP with fairly high molecular mass and good elastomeric and strength characteristics. An increase in the monomer concentration, all other conditions being the same, induces an increase in the molecular mass and some decrease in the content of isotactic pentads (see Table 2, rows 6, 8 and 9, 10). Note that in the presence of titanium metallocenes of this type, elSBPP is formed only in a narrow temperature range, 25 to 30 °C.[55] At −25 °C, the content of isotactic pentads reaches 72% (see Table 2, row 2). In addition, titanium complexes are much less stable than zirconium and hafnium analogs. Hafnium complexes give rise to PP with higher molecular masses than zirconocenes (see Table 2, rows 4, 6 and 5, 9); this is typical of metallocene catalysis. An unusual feature is that the activities of zirconocenes and hafnocenes are comparable. In the case of hafnium complexes, all other factors being the same, PP samples with higher degrees of isotacticity are formed (see Table 2, rows 4, 6 and 5, 9). The replacement of the propylidene bridging groups by dimethylsilylene groups results in an increase in the molecular mass and isotacticity of the PP (see Table 2, rows 6, 9; 7, 10 and 8, 11). An increase in the monomer concentration is accompanied by a decrease in the isotacticity of the polymer for both hafnium and zirconium catalysts (see Table 2, rows 6, 7 and 9, 10), whereas an increase in the reaction temperature from 0 to 25 °C markedly decreases the isotacticity of the PP formed with the hafnium complex (see Table 2, rows 11, 10).

In a study of a stereoblock polymer prepared by anionic polymerisation of acrylates, an idea was put forward that two different states of the AC, aspecific (non-selective) and isospecific ones, may exist.[60] Subsequently, these views have been often used as the basis of the mechanisms of formation of stereoblock PP, in particular for the catalysts of C_1 symmetry.[51–58] The key feature of asymmetric *ansa*-metallocenes is the presence of two inequivalent vacancies in the AC accessible for the monomer coordination and growth of the polymer chain. Usually, one vacancy is aspecific (non-selective) and the other one is isospecific. Chien and Collins explained the formation of a sequence of atactic and isotactic blocks in the presence of these catalysts in terms of models which take into account polymer chain growth in the active centre (the small square shows a coordination vacancy), whose stereospecific action changes as a result of slow (see Refs 51–55) or fast (see Refs 56–58) inversion (on the time scale of olefin coordination and addition), for example, due to migration of the polymer chain (P).



Aspecific state Isospecific state

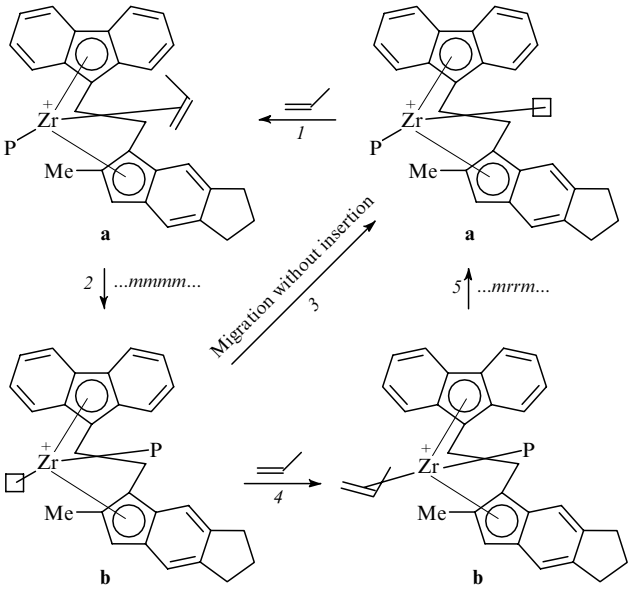
According to the Chien model, several steps of olefin coordination and insertion occur in turn in either of the active sites until its inversion takes place. However, within the framework of this model, it is difficult to explain the decrease in the content of the *mmmm* pentads following an increase in the monomer concentration on structurally similar Collins complexes. In conformity with the Collins model, the monomer is randomly coordinated

and inserted at the first or second accessible reactive active site. When two competing reactions are involved, namely, olefin insertion and chain isomerisation (migration without insertion), short isotactic sequences would regularly arise in the macromolecule; this would determine the elastomeric properties of the resulting PP; the length of these sequences would depend on the type of the coordination vacancies and the ratio of the chain growth rates in each site to the rate of active centre isomerisation. This model is also supported by the fact that hafnium complexes exhibit more pronounced stereocontrol action than the zirconium analogues, all other conditions being the same. The rate of polymer chain growth for hafnocenes is much lower than that for zirconocenes. Within the framework of this model, the replacement of zirconium by hafnium can result in a decrease in the ratio of the chain growth rate to the inversion rate.

A similar mechanism of the action of complexes with C_1 symmetry assuming the presence of two sites with different stereospecificities and competition between chain growth and migration without insertion (which also gives rise to elSBPP) has been proposed recently [59,61] for a series of structurally rigid zirconocenes **8**–**15**.

A characteristic feature of these zirconocenes, as noted above, is 'stereoduality', *i.e.*, the existence of two different coordination vacancies **a** and **b** (Scheme 1, small squares) in the cationic metal alkyl active site formed under the action of MAO.

Scheme 1



The non-selective coordination vacancy **b** is sterically less crowded than the isospecific vacancy **a**, and the processes of monomer coordination and chain migration to coordination vacancy **b** without insertion compete in the active centre. When the monomer concentration is low, chain migration without insertion can kinetically predominate. In this case, the reactions 'monomer insertion at vacancy **a** with chain migration (**a** → **b**) and subsequent chain migration without insertion (**b** → **a**)' will result in the formation of ...*mmmm*... sequences (see Scheme 1, cycle *1* → *2* → *3*). When the monomer concentration increases, the probability of coordination and insertion at the sterically less hindered vacancy **b** becomes higher. The chain migration to the monomer that has added non-selectively gives rise to 'errors,' which are 'corrected' at the next step of monomer addition at vacancy **a**, and the...*mrrm*.... sequences are thus formed (see Scheme 1, cycle *4* → *5* → *1*). This type of polymer chain growth virtually excludes the propagation of 'errors' and, depending on the conditions, it can result in alternation of short isotactic sequences separated by single stereodefects. Polypropylene formed by this mechanism is an isotactic macromolecule divided into short continuous isotactic segments by regularly arising 'errors' (see Fig. 2 *c*, elSBPP with $k = 1$).

An increase in the polymerisation temperature and a decrease in the monomer concentration lead to a relative increase in the rate of chain migration without insertion and, correspondingly, to a higher content of isotactic pentads (see Table 2, rows 13, 14; 16, 17; 12, 13 and 15, 16). Conversely, an increase in the monomer concentration increases the probability of monomer insertion at coordination vacancy **b**, resulting in a decrease in isotacticity. It will be shown below that, in conformity with the proposed mechanism, the PP samples prepared with these catalyst systems are characterised by either the absence or low content of pentads of the ...*rmrm*... type with double 'errors'.[61]

It was also found for these types of catalyst systems that no 'errors' caused by isomerisation of the growing chain unit attached to the catalyst *via* β-hydride shift or the formation of allylic intermediates, typical of catalysts with C_2 symmetry,[62–66] arise in this case. The absence of these reactions was confirmed experimentally by analysis of the pentad composition of the PP synthesised by polymerisation of $CH_2=CDMe$.[59]

The catalysts of C_1 symmetry substituted at the 2-position make it possible to prepare PP with a very broad range of properties. Some parameters of the resulting polymers are presented in Table 2. An increase in the monomer concentration entails an increase in the molecular mass and a decrease in the content of isotactic pentads and in the degree of crystallinity of the polymer, while an increase in the reaction temperature is accompanied by lowering of the polymer molecular mass and an increase in the crystallinity. The best catalysts are 2-methyl-substituted complexes **8**–**10** with ethylene bridges because they exhibit high activity and ensure the formation of elSBPP with a relatively high molecular mass and a content of isotactic pentads at a level of 30%–50%.

These catalyst systems allow effective preparation of PP the properties of which vary over very broad limits, from those typical of highly crystalline rigid thermoplastics to those peculiar to low-crystallinity elastomers, which behave as viscous liquids under the action of load (Fig. 6). The samples combining high molecular mass ($\sim$200 000 g mol^{-1}) and moderate isotacticity ([*mmmm*] = 30%–40%) display good elastomeric and strength properties. The elongation at rupture for some samples reaches 1700%–2000%. However, a characteristic feature of elSBPP prepared on catalysts with C_1 symmetry is a relatively low melting

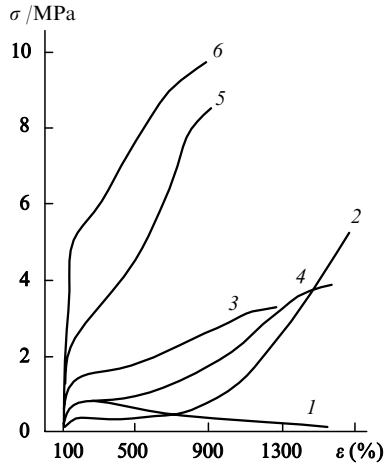


Figure 6. Drawing curves of PP samples prepared on the **10**–MAO catalyst system and exhibiting properties of viscoelastic (*1*), elastomeric (*2*–*4*) and stiff thermoplastics (*5*, *6*).[59]
M_w (g mol^{-1}): (*1*) 134 000; (*2*) 170 000; (*3*) 96 000; (*4*) 63 000; (*5*) 48 000; (*6*) 48 000.
[*mmmm*] (%): (*1*) 20; (*2*) 37; (*3*) 38; (*4*) 37; (*5*) 60; (*6*) 57.

point.[59] This indicates the presence of a substantial number of regiodefects in the polymer chain.

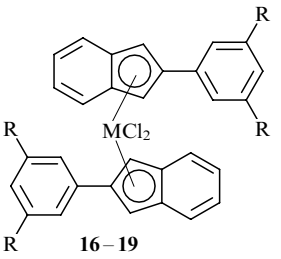
New metallocene complexes of C_1 symmetry for the synthesis of elastomeric PP have been described.[26] These *ansa*-metallocenes with strap-type $-(CH)_2-$ or $-(CH_2)_2-$ substituents at the 4- and 5-positions of the fluorenyl ligand possess high activity, 20–70 kg PP (g Cat.)$^{-1}$ h^{-1} or 1–5 kg PP (mmol M)$^{-1}$ [C_3H_6]$^{-1}$ h^{-1} (polymerisation in the liquid monomer medium); they provide the synthesis of PP with a molecular mass of 8×10^4 to 1.4×10^6 g mol^{-1} and ensure very good elastomeric properties. Indeed, the residual elongation after stretching the sample by 300% is only 2.5%–10.0%. The greatest observed elongation of the sample reaches 5200%, the tensile strength is 0.8–2.5 MPa, and Young's modulus is 2.1–9.0 MPa. It has been assumed [26] that the unique properties of elSBPP prepared with these catalysts are determined by ultrasmall (nano-sized) crystallites which form the junctions of the polymer network.

A criterion of a 'good catalyst' of this new type for the synthesis of elastomeric PP has been proposed,[26] determined by the ratio between the parameters of the catalyst asymmetry (ratio of the van der Waals areas of the larger ligand and the smaller one) and parameters of stereorgularity of the synthesised PP (the ratio of *mm*- to *rr*-triads). The proportion of the *mmmm* pentads in the resulting polymers does not exceed 31%; however, unlike elSBPP formed in the presence of C_1-symmetric catalysts considered above, these polymers contain substantial numbers of syndiotactic pentads ([*rrrr*] $\approx$ 28%).

b. The 'bis(2-substituted indenyl) metallocene – polymethylaluminoxane' catalyst systems

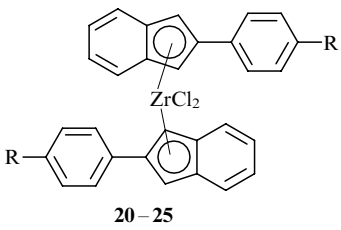
Bisindenyl metallocenes with aryl (**16**–**25**) and alkyl (**26**–**29**) substituents at the 2-position of the indenyl ring represent the most extensive and thoroughly studied class of metallocenes effective in the synthesis of elSBPP. In recent years, this series has been extended by zirconocenes with mixed hapto-bonded (**30**–**35**) and heterocyclic (**36**–**38**) ligands. Due to the intensive research, one can expect that new catalyst systems of this class effective in the synthesis of stereoblock PP would appear in the near future.

The 2-aryl-substituted dichloride complexes **16**, **19** were the first of the series of 'oscillating' metallocenes.[67–72] Upon activation with MAO, these catalysts ensure the formation of stereoblock PP with high molecular masses.



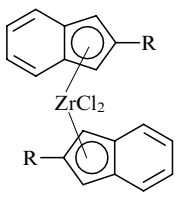
16–**19**

M = Zr: R = H (**16**), Me (**17**), CF_3 (**18**); M = Hf, R = H (**19**).



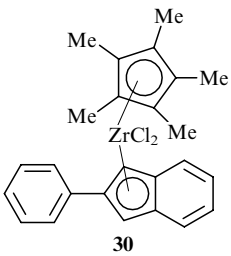
20–**25**

R = Me (**20**), Et (**21**), Bu^n (**22**), $SiMe_3$ (**23**), CF_3 (**24**), Cl (**25**).

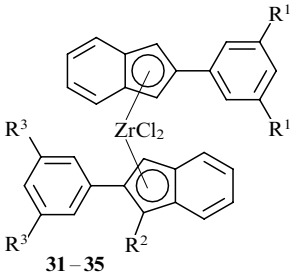


26–**29**

R = Me (**26**), Bu^n (**27**), cyclo-C_6H_{11} (**28**), Bn (**29**).

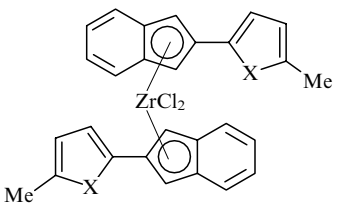


30



31–**35**

$R^1 = R^2 = H$, $R^3 = CF_3$ (**31**);
$R^1 = R^3 = H$, $R^2 = Me$ (**32**);
$R^1 = H$, $R^2 = Me$, $R^3 = CF_3$ (**33**);
$R^1 = CF_3$, $R^2 = H$, $R^3 = Me$ (**34**);
$R^1 = R^3 = CF_3$, $R^2 = Me$ (**35**).

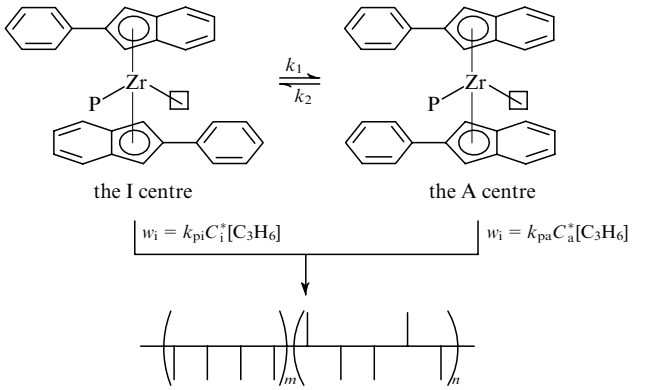


36–**38**

X = O (**36**), S (**37**), NMe (**38**).

X-Ray diffraction studies [67, 73–75] showed that both the zirconocene **16** and the hafnocene **19** exist as two rotation isomers relative to the metal–hapto-ligand bond in the crystal unit cell. This attests to the energetic equivalence of both forms. This fact served as a pre-requisite for the proposed [67] 'oscillation' mechanism of the formation of stereoblock PP on catalysts of this type (Scheme 2, where the I and A stand for the isospecific and aspecific centres, respectively, k_{pi} and k_{pa} are the rate constants for polymerisation at the I and A centres, C_i^* and C_a^* are the concentrations of the I and A centres; and w_i and w_a are the rates of chain growth at the I and A centres, respectively).

Scheme 2



It was assumed that during polymerisation, the active cationic alkyl metal complex retains the ability to undergo barrier-free rotation. During the growth of the polymer chain, reversible isomerisation of the complex from the isospecific *rac*-form to the aspecific *meso*-form takes place repeatedly. The insertion of propylene during the period of existence of the *rac*-form of the active centre (the I centre) gives rise to isotactic sequences. On the *meso*-form of AC (the A centre), propylene insertion yields atactic blocks. To obtain the stereoblock structure of the polymer, it is necessary that the isomerisation rate be lower than the rate of olefin insertion but higher than the chain growth rate. Thus, chain growth on the 'oscillating' type AC gives macromolecules of the stereoblock structure. The length of the isotactic sequences is usually rather small and the stereoblock PP synthesised under the action of these metallocenes is distinguished by a low degree of crystallinity with a rather high molecular mass.

For a large number of complexes of this type, the influence of polymerisation conditions on the catalyst activity and characteristics of the resulting polymers (microstructure and fractional composition, molecular mass, MMD, elasticity) has been studied.[67, 70, 72, 73, 76–78] Typical properties of catalyst systems and elSBPP prepared on these catalysts, and their dependence on the reaction conditions are presented in Table 3.

Table 3. Polymerisation of propylene induced by 'oscillating' catalysts (MAO cocatalyst).

Row	Complex	Al : Zr	$p_{C_3H_6}$ /atm	T_p /°C	A	$10^{-3} M_w$ /g mol^{-1}	$M_w : M_n$	[*mmmm*] (%)	Ref.
1	**16**	1000	see [a]	0	0.20	556	2.8	38	76
2	**16**	2200	see [a]	8	0.10	411	4.0	29	70
3	**16**	1000	see [a]	20	0.19	539	4.7	39	76
4	**16**	1000	see [a]	40	0.35	163	3.4	30	76
5	**20**	1840	see [a]	30	0.18	360	4.5	–	72
6	**20**	1550	see [a]	50	0.40	37	2.6	30	72
7	**16**	4800	see [a]	30	0.54	145	3.0	31	70
8	**16**	10 000	see [a]	20	1.02	549	3.5	–	79
9	**16**	31 600	see [a]	20	1.77	236	2.4	16	80
10	**19**	1000	2.5	20	0.54	345	2.3	8	73
11	**16**	1000	2.5	20	0.50	232	3.8	23	73
12	**19**	1000	7.0	20	0.21	486	2.1	9	73
13	**16**	1000	7.0	20	0.17	435	3.0	31	73
14	**18**	1000	6.3	25	0.37	332	3.7	73	68
15	**16**	1000	1.8	25	0.32	179	3.0	20	68
16	**16**	1000	3.5	25	0.36	241	3.5	26	68
17	**16**	1000	6.3	25	0.54	369	3.9	32	68
18	**26**	3500	1.0	−20	0.03	600	3.5	11	81
19	**27**	3500	1.0	−20	0.004	260	2.1	16	81

Note. The catalyst concentration was varied in the range of 10^{-5}–10^{-6} mol litre^{-1}. [a] Polymerisation was carried out in the liquid monomer.

The catalyst systems in question are characterised by a slight increase in the activity and a sharp decrease in the molecular masses with an increase in polymerisation temperature [67, 70, 72, 73, 76–78] (see, for example, Table 3, rows 1, 4 and 2, 7). The temperature at which a high-molecular-mass elSBPP can be prepared usually does not exceed 30–40 °C. It has been noted [70] that the yield of the solid polymer formed upon polymerisation in the liquid monomer medium at 50 °C equals 30% based on the monomer consumed; the rest falls to low-molecular-mass products. The same sharp decrease in the molecular mass of the polymer upon an increase in the reaction temperature has been observed [72] for the **20**–MAO catalyst system, which induces the formation of elSBPP with a higher molecular mass and a higher degree of crystallinity (see Table 3, rows 5, 6). From the temperature dependence of the activity of the complex **16** (liquid propylene, 0–40 °C) measured in several studies,[70–72] the effective activation energy of polymerisation was found to be $E_a \approx 4$ kcal mol^{-1}.

Unlike a number of other metallocene catalyst systems, for these complexes, a marked decrease in the polymerisation rate with time was observed, even for low reaction temperatures (Fig. 7).[72] The activity of catalyst systems and the molecular-mass characteristics of elSBPP largely depend on the method used to prepare the catalyst.[70, 73, 80] In many cases, the resulting polymers are characterised by a broad MMD ($M_w : M_n = 3$–6) and can be separated into several fractions by extraction with boiling ether and n-heptane. It is of interest that the differences in molecular masses and stereoisomeric compositions of the fractions prepared in the presence of these catalyst systems are much smaller than those obtained with the use of isospecific heterogeneous catalysts.[82, 83] Comparison of the data obtained by different researchers [70, 79, 80] allows the conclusion that the activity of complexes of this type increases with an increase in the Al : Zr ratio (see Table 3, rows 3, 7–9), which is typical of catalyst systems based on metallocenes.

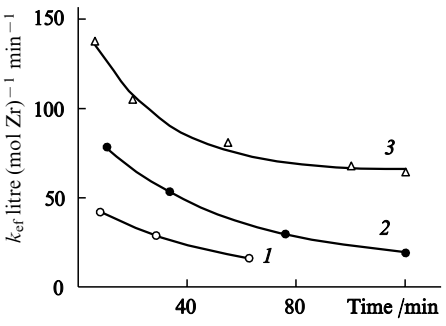


Figure 7. Effect of conditions of propylene polymerisation on the variation of the catalytic activity of the **16**–MAO system with time.[70] Polymerisation was carried out in the liquid monomer medium; $k_{ef} = w_p[C_3H_6]^{-1}[M]^{-1}$, where w_p is the rate of polymerisation. T_p (°C): (*1*) 2; (*2*) 8; (*3*) 30.

An interesting feature of these catalysts is that the activities of the zirconium and hafnium complexes **16** and **19** are comparable.[69, 72, 73] As noted above, hafnocenes with C_1 symmetry behave in a similar way.[56–58] Normally, hafnium metallocenes of other types are much less active than zirconium analogues, all other factors being the same, and give polymers with much higher molecular masses. The 2-phenyl-substituted complexes **16**, **19** have approximately equal activities; in the case of elSBPP prepared on the hafnium complex, the molecular mass is higher and the polydispersity and the degree of isotacticity are much lower than those for elSBPP synthesised under the action of zirconium analogue (see, for example, Table 3, rows 11, 10 and 13, 12). Bruce *et al.*[73] believe that the comparable levels of activity of the complexes **16** and **19** are due to the more effective formation of AC in the case of the hafnium catalyst.

A number of publications have been devoted to the analysis of the influence of substituents on the catalytic properties of 2-aryl-substituted complexes and characteristics of the resulting elSBPP. The introduction of methyl substituents at the 3- and 5-positions of the benzene ring (complex **17**) causes some decrease in the catalyst activity and the polymer molecular mass; in addition, the isotacticity of the polymer substantially decreases.[68, 69] The complex **18** containing trifluoromethyl substituents provides the formation of a crystalline PP (see Table 3, row 14). It is of interest that polymers prepared under the action of the complexes **16**–**18**, even with different contents of isotactic pentads, have rather high melting points (140–150 °C), which implies a small number of regiodefects in isotactic blocks. The introduction of various substituents into the *para*-position of the benzene ring (complexes

20–**25**) barely affects the activity of the system and the properties of the elSBPP formed.[72,78] Both *rac*- and *meso*-forms of the analogue of the complex **16** with the methyl substituent at the 1-position give rise to an amorphous low-molecular-mass PP with very high polydispersity coefficients, $M_w : M_n = 4-15$.[84] The elSBPP formed under the action of the complex **30** is close in stereochemical composition to the polymer formed with the **16**–MAO catalyst system; however, regarding the melting point and the macrotacticity index, it is close to the elSBPP prepared on catalysts with C_1 symmetry.[71] Complexes **31**–**35** with mixed ligands and different substituents are less active catalysts than the bisindenyl complexes with identical ligands.[85]

The main channel of chain transfer by the catalyst systems considered is the transfer of the β-hydrogen atom to the metal and the coordinated monomer.[80] An interesting feature of 2-arylindenyl systems is the clear-cut effect of the co-monomer, which was identified in a study of propylene copolymerisation with ethylene induced by the complexes **16** and **18**.[79,86] The activity of the catalyst system increases 2- to 8-fold even at a low ethylene : propylene molar ratio (0.05–0.08) in the monomer mixture. The increase in the activity is accompanied by a substantial (2–3-fold) increase in the molecular mass of the copolymer. The ethylene content in the copolymer varies in the range of 15 mol %–50 mol %. The system activity also increases appreciably upon the introduction of hydrogen. It has been assumed[86,87] that the co-monomer effect shows itself as the ability of ethylene to be inserted and to 'wake up' the AC after the formation of a regiodefect of the polymer chain as a result of the monomer 2,1-addition.

Studies of the complexes **16** and **18** showed[87] that they are more regiospecific than the isospecific $EtInd_2ZrCl_2$ catalyst (Ind is indenyl). The non-bridged complex **16** produces PP containing 0.1 mol %–0.3 mol % of 2,1-added units. It is of interest that 'regioerrors' are detected only in isotactic sequences of the polymer, *i.e.*, they arise only in those cases where the 'oscillating' metallocene occurs in the isospecific state. This is confirmed by the fact that no 'errors' are found in the PP synthesised by the polymerisation of propylene in the presence of *meso*-$Me_2Si(2\text{-PhInd})_2ZrCl_2$, whereas the *rac*-analogue of this complex produces PP with 'errors' caused by the 3,1-addition.[88]

A specific feature of the 'oscillating' catalysts is an increase in the content of the *mmmm* pentads following an increase in the monomer concentration (see, for example, Table 3, rows 15–17). Quantitative analysis of this phenomenon is based on the fact that the rate of polymerisation is proportional to the monomer concentration, while the rate of isomerisation does not depend on it and, since the content of isotactic pentads is determined by the ratio of the rates of these reactions, the regularity of the polymer increases with an increase in the monomer concentration. This has been observed in numerous experiments.[67–69,73,78] As discussed above, an opposite dependence of the content of isotactic pentads on the monomer concentration was found for metallocenes with C_1 symmetry.

A mathematical model has been proposed to describe the oscillation mechanism of polymer chain growth.[80,89,90] Computer generation of PP macromolecules has been carried out with variation of three parameters, namely, the stereoselectivity of the isospecific active centre (α), the selectivity of the aspecific centre (β) and the g/K parameter, which specifies the ratio of the relative reactivity to the stability for iso- and aspecific states ($g = k_{pa}/k_{pi}$, $K = k_1/k_2$). Thus $g/K > 1$ corresponds to the predominant existence of the isospecific AC. The dependence on the pentad composition on the monomer concentration for definite α, β and g/K values is determined by the parameter

$$\Delta = \frac{(k_{pi}/k_1 + k_{pa}/k_2)[C_3H_6]}{2}.$$

The best agreement between experimental and calculated pentad compositions was found for $\alpha = 0.97$, $\beta = 0.56$ and $g/K = 0.6$. The Δ parameter varies in the 1–10 range as the propylene concentration changes from 1.2 to 11 mol litre^{-1}. However, the authors of the model admit[80] that the same kinetic dependence of the pentad composition on the monomer concentration can be described qualitatively and quantitatively by the Busico model,[63,64,91] which takes into account the competition between the chain growth and epimerisation processes with the assumption that the AC have two active vacancies accessible for monomer coordination and the polymer chain growth.

Since the model of the 'oscillating' complex is widely recognised, several factors deserve attention, both those confirming the proposed mechanism and those conflicting with it. The mechanism in question is supported by the increase in the content of the *mmmm* pentads with an increase in the monomer concentration, which was observed experimentally for these complexes. The mathematical model describing this mechanism provides a quantitative correspondence between the polymer microstructures calculated and found experimentally depending on the polymerisation conditions (monomer concentration, temperatures) for reliable values of model parameters. The X-ray diffraction data for the complexes **16**, **19** are also a forcible argument in favour of the 'oscillating' complex. Theoretical studies[92,93] demonstrated the presence of two energy minima for the transition state corresponding to the *rac*- and *meso*-forms of the complex **16** and stabilised by the π-interactions between the phenyl substituents and the aromatic system of the indenyl ligands (π-stacking interactions); the two minima are energetically equivalent ($\Delta\Delta H = 0.6$ kcal mol^{-1}). Indeed, on passing to hydrogenated analogues of the complex **16**, $(2\text{-CyInd})_2ZrCl_2$ (Cy is cyclohexyl), $(2\text{-Ph-H}_4\text{Ind})(2\text{-PhInd})ZrCl_2$ and $(2\text{-Cy-H}_4\text{Ind})_2ZrCl_2$, all other factors being the same, a substantial decrease in the PP isotacticity has been noted: [*mmmm*] = 32%, 15%, 13% and 5%, respectively.[77]

Direct investigation of isomerisation processes for 'oscillating' catalysts is of interest. The data of dynamic NMR for $(2\text{-PhInd})_2HfBn_2$ (see Ref. 73) and structurally related (2-phenylcyclopenta[*l*]phenanthryl)$_2ZrCl_2$ (see Ref. 94) indicate a very high frequency of rotation of hapto-bonded ligands: 6800 s^{-1} for the former complex and $\sim 1 \times 10^8$ s^{-1} for the latter one. The latter zirconocene activated by MAO ensures (although with a low activity) the formation of a low-molecular-mass PP similar in stereoisomeric composition to the elSBPP prepared under the action of the complex **16**. The frequencies of ligand rotation about the axis passing through the M atom and the centroid of the Cp ring are several orders of magnitude greater than the frequency of olefin insertion estimated from the maximum rate of monomer absorption, which equals 0.1–10.0 insertions of C_3H_6 per second even with allowance for the low efficiency of the formation of AC. Evidently, such a fast rotation should average the stereospecific action of the AC and ensure the formation of PP with a narrow MMD. No data on the rate of isomerisation in real catalyst systems (MAO-activated metallocenes) are available. To explain the observed contradiction, it has been suggested[94] that the chain growth actually proceeds at a very high rate, which exceeds the rate of rotation of the hapto-bonded ligands but during the period of growth of the macromolecules, the AC pass many times into the 'dormant' state, perhaps, due to the formation of a contact ion pair with the counter-ion.

Note that only for the complexes **16** and **19**, was the existence of two energetically equivalent stereoisomers identified. Data from X-ray diffraction analyses of a number of other complexes which catalyse the formation of stereoblock PP indicate the presence of only one stereoisomer, for example, the *meso*-form of the complex **17**,[68] the *rac*-form of the complex **18**[68,73] and its hafnium analogue[73] and the *meso*-form of the complex **21**,[78] which does not differ from the complex **16** in catalytic properties.

Although ^{13}C NMR spectroscopy is a unique tool for analysing the structure of the polymer chain and, correspondingly, the catalytic properties of the AC, which allows one to evaluate its stereo- and regiospecificity, the stereocontrol mechanisms and so

on,[34–37, 39, 40, 41, 95] this method still does not provide sufficient information for the analysis of the contents of sequences comprising 15–16 monomer units capable of crystallisation.

In the opinion of Gauthier and Collins,[56, 58] the known data on the microstructure of elSBPP do not allow one to decide unambiguously in favour of one or another statistic model. For example, elSBPP formed under the action of the **19**–MAO catalyst system [72] has a pentad composition that can be obtained by mathematical generation of the polymer chain in terms of the Bernoullian model with a probability of *m*-addition (p_m) equal to 0.58. However, no correspondence was attained between the calculated and experimental compositions for polymers with higher contents of isotactic pentads, which also exhibit elastomeric properties; this indicates that the given model is inapplicable to the description of the real mechanism of formation of stereoblock PP. Nevertheless, the possibility of existence of catalyst systems which form stereoblocks also by this mechanism cannot be ruled out completely.

A finding quite unusual for metallocene catalysis is that PP samples prepared by virtue of 'oscillating' catalyst systems are characterised in some cases by high polydispersity values $M_w : M_n$ (Tables 3, 4). The correlation between the degree of isotacticity and the polydispersity of PP was first pointed out by Bruce *et al.*[73] This can be illustrated by the plots shown in Fig. 8 for the PP samples prepared using the [2-(4-RC_6H_4)Ind]$_2MCl_2$ and [2-(3,5-$R_2C_6H_3$)Ind]$_2MCl_2$ complexes with the MAO cocatalyst (Al : Zr = 1000) at 20–25 °C.[68, 69, 73, 78] An increase in the polydispersity with an increase in the isotacticity can be followed in Fig. 8 for each type of complex. The hafnium analogues catalyse the formation of PP with a much lower crystallinity and polydispersity. Since the content of isotactic pentads is determined by the isospecific state of complexes of C_{2v} symmetry and can be regarded as a measure of activity, it is reasonable to suggest that this state is realised upon reversible coordination of a component (or components) of the reaction mixture (MAO, $AlMe_3$, solvent, monomer) by the cationic alkyl metal complex. These interactions might be responsible for broadening of the MMD of the elSBPP samples prepared in the presence of the catalyst systems.

In this connection, the following example is of interest. It has been reported [82] that the elastomeric PP prepared in the presence of hydrogen (0.044 mmol of H_2 per mole of C_3H_6) in order to decrease the molecular mass differs appreciably from the elSBPP produced in the absence of hydrogen, all other conditions being the same (liquid propylene, 23 °C). The molecular mass of the product decreases and the polymer synthesised in the presence of hydrogen has the following composition: 72% of ether-soluble fraction, 13% of heptane-soluble fraction and 15% of a fraction insoluble in heptane, whereas the fractional composition of the polymer obtained without hydrogen is completely different: 36%, 43% and 21%, respectively. The microstructures of the fractions are also markedly different, the isotacticity of all fractions being much higher in the case of the polymer prepared in the presence of hydrogen (Table 5, rows 11–14, 15–18).

Table 4. Strain and elastic pproperties of elSBPP prepared under the action of bis(2-alkylindenyl)zirconium dichlorides in the presence of the MAO cocatalyst (T_p = −20 °C, toluene, $p_{C_3H_6}$ = 1 atm, Al : Zr = 3500).[96, 97]

Parameter	**26**	**27**	**29**	**36**
M_w /g mol^{-1}	600 000	260 000	90 000	720 000
$M_w : M_n$	3.5	2.1	2.6	2.8
[*mmmm*] (%)	10	16	26	19
Tensile strength /MPa	2.4	6.85	0.55	–
Elongation at rupture (%)	1224	1109	1085	839
Modulus of elasticity /MPa	0.98	1.04	0.04	–
Stress at 100% elongation /MPa	0.81	0.86	0.24	0.77
Recovery after 100% elongation (%)	93	95.3	77.3	94
Stress at 300% elongation /MPa	1.07	1.13	0.25	0.76
Recovery after 300% elongation (%)	95.1	95.7	70.2	81

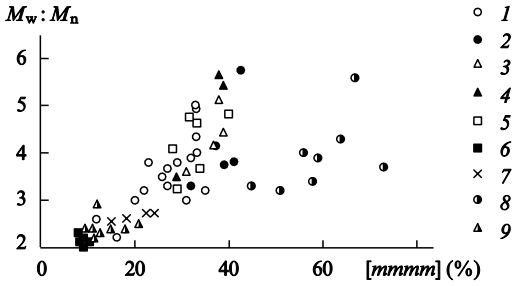


Figure 8. Polydispersity *vs.* isotacticity for PP samples prepared on 'oscillating' catalysts activated by MAO at 20–25 °C.[68, 69, 73, 78] Catalyst: (*1*) **16**; (*2*) **20**; (*3*) **21**; (*4*) **22**; (*5*) [2-(4-Bu^{t}C$_6$H$_4$)Ind]$_2$ZrCl$_2$; (*6*) **19**; (*7*) **17**; (*8*) **18**; (*9*) hafnium analogue of the complex **18**.

In a recent study,[80] it was reported that the synthesis of PP induced by the complex **16** can yield elSBPP with a narrow MMD ($M_w : M_n$ = 2.1–2.7). However, the polymerisation procedure employed in this study [80] results, with other conditions remaining the same, the formation of a PP in which the molecular mass is 2–4 times lower than that reported previously. The observed extension of the MMD was attributed [80] to the increase in the polymerisation rate following an increase in the monomer concentration and by a decrease in the rate of mass transfer and propylene solubility during polymerisation at high rates.

The catalytic properties of 2-alkyl-substituted complexes **26**–**29** in the propylene polymerisation in toluene have been studied.[81, 96] At a propylene pressure equal to 1 atm, elSBPP with a rather high molecular mass can be formed only at low temperatures (−20, 0 °C). Thus at −20 °C, elSBPP with a molecular mass of 600 000 g mol^{-1} is formed under the action of the complex **26**. When more active catalysts are used, PP with a higher molecular mass is produced. The maximum activity is exhibited by the complexes **26** and **27** (see Table 3, rows 18, 19). The specific activity of the complex **26** is four times lower than that of the complex **16** at 0 °C. The activity of catalysts in propylene polymerisation increases 1.3–2.3-fold as the reaction temperature decreases from 0 to −20 °C. All 2-alkyl-substituted complexes, except for compound **26**, are inactive in ethylene polymerisation at low temperatures. Similar properties are found for complexes **36** and **37** with heterocyclic substituents at the 2-position in the presence of the MAO cocatalyst:[97] high-molecular-mass elastomeric SBPP is formed on these catalysts only at low temperatures (0, −20 °C); the catalyst activity increases as the reaction temperature decreases; and more active catalysts give rise to elSBPP with a higher molecular mass. Thus the activity of complex **38** at −20 °C equals 59 kg PP (mol Zr)$^{-1}$ h^{-1} atm^{-1}, and the weight-average molecular mass of the resulting PP is 3600 g mol^{-1}. Meanwhile, under similar conditions, complex **36** exhibits an activity comparable to that of the complex **16** and leads to the formation of PP with a molecular mass of 720 000 g mol^{-1}. Dynamic NMR analysis of **36** and **37** identified fast rotation around the axis that passes through the Zr atom and the centroid of the Cp ring and the presence of a conformational equilibrium, fast on the NMR time scale, although an X-ray diffraction investigation of the complex **36** indicated that only *meso*-**36** exists in the solid state,[97] unlike the situation with the complex **16**. It can be demonstrated in relation to the elSBPP prepared with the complexes **26**, **27**, **29** and **36** that the isotacticity–molecular mass combination of properties is important for the strength and elastomeric characteristics of the polymer (see Table 4).

Table 5. Pentad composition of the elSBPP samples prepared using homogeneous catalyst systems.

Row	Catalyst	T_p /°C	$p_{C_3H_6}$ /atm	[*mmmm*]	[*mmmr*]	[*rmmr*]	[*mmrr*]	[*mrmm* + + *rmrr*]	[*rmrm*]	[*rrrr*]	[*rrrm*]	[*mrrm*]	n_{iso} (see [a])	Ref.
1	**5** – MAO	0	1	0.39	0.17	0.03	0.19	0.06	0.02	0.02	0.04	0.09	8.6	58
2	**5** – MAO	25	1	0.37	0.19	0.03	0.19	0.07	0.02	0.02	0.03	0.09	8.1	58
3	**5** – MAO	25	3	0.32	0.18	0.03	0.20	0.08	0.02	0.04	0.05	0.09	7.5	58
4	**7** – MAO	25	1	0.53	0.16	0.02	0.14	0.04	0.02	0.01	0.02	0.06	10.7	56
5	**7** – MAO	25	4	0.50	0.16	0.03	0.13	0.06	0.03	0.01	0.02	0.06	10.2	58
6	**10** – MAO	30	2	0.43	0.18	0.02	0.20	0.03	–	0.02	0.03	0.10	8.9	59
7	**10** – MAO	30	10	0.25	0.17	0.03	0.22	0.09	–	0.06	0.09	0.10	6.9	59
8	**10** – MAO	50	8	0.49	0.16	0.02	0.18	0.03	–	0.02	0.02	0.09	10.3	59
9	**16** – MAO	8	see [b]	0.29	0.15	0.05	0.14	0.16	0.08	0.03	0.07	0.03	7.9	70
10	**16** – MAO	30	see [b]	0.31	0.15	0.06	0.13	0.16	0.08	0.03	0.05	0.04	8.2	70
11	**16** – MAO [c]	23	see [b]	0.32	0.15	0.04	0.10	0.18	0.09	0.02	0.05	0.05	8.4	82
12	**16** – MAO [d]	23	see [b]	0.18	0.16	0.06	0.12	0.22	0.11	0.03	0.08	0.05	6.3	82
13	**16** – MAO [e]	23	see [b]	0.33	0.16	0.05	0.11	0.18	0.08	0.02	0.05	0.04	8.2	82
14	**16** – MAO [f]	23	see [b]	0.51	0.13	0.03	0.07	0.13	0.06	0.01	0.04	0.04	12.1	82
15	**16** – MAO [g]	23	see [b]	0.34	0.14	0.04	0.09	0.16	0.08	0.02	0.06	0.06	8.8	82
16	**16** – MAO [h]	23	see [b]	0.23	0.17	0.05	0.12	0.20	0.09	0.03	0.05	0.06	6.7	82
17	**16** – MAO [i]	23	see [b]	0.53	0.13	0.02	0.09	0.11	0.05	0.01	0.03	0.04	12.5	82
18	**16** – MAO [j]	23	see [b]	0.81	0.07	0.01	0.04	0.04	0.01		0.01	0.02	28.9	82
19	**19** – MAO	30	see [b]	0.12	0.15	0.07	0.12	0.25	0.13	0.03	0.08	0.06	5.6	72
20	**20** – MAO	30	see [b]	0.36	0.14	0.06	0.10	0.16	0.08	0.02	0.05	0.03	9.3	72
21	**27** – MAO	−20	1	0.16	0.17	0.08	0.12	0.20	0.11	0.04	0.06	0.06	5.9	96
22	R_2ZrMe_2 – $AlBu^i_3$ (see [k])	30	see [b]	0.27	0.14	0.07	0.14	0.16	0.08	0.04	0.08	0.04	7.9	98
23	R_2ZrMe_2 – $AlBu^i_3$ (see [l])	30	4	0.49	0.14	0.03	0.10	0.11	0.05	0.01	0.03	0.03	11.0	98
24	R_2ZrMe_2 – $AlBu^i_3$ (see [m])	30	4	0.18	0.18	0.07	0.15	0.18	0.09	0.04	0.07	0.07	6.0	98
25	$(acac)_2ZrCl_2$ – MAO [n]	0	6	0.28	0.12	–	0.12	0.15	0.08	0.06	0.11	0.09	8.7	99

[a] Effective length of isotactic sequences estimated from the content of the corresponding pentads: $n_{iso} = 4 + 2[mmmm]/[mmmr]$ (see Ref. 47). [b] Polymerisation was carried out in the liquid monomer. [c] Non-fractionated elSBPP prepared on the **16** – MAO catalyst system (Al : Zr = 1000). [d] Ether-soluble fraction (36%). [e] Heptane-soluble fraction (43%). [f] Fraction insoluble in boiling heptane (21%). [g] Non-fractionated elSBPP prepared on the **16** – MAO catalyst system (Al : Zr = 1000) in the presence of hydrogen (0.044 mol H_2 per mol C_3H_6). [h] Ether-soluble fraction (72%). [i] Heptane-soluble fraction (13%). [j] Fraction insoluble in boiling heptane (15%). [k] R = 2-PhInd, Al : Zr = 120. [l] Polymerisartion was carried out in toluene, $p_{C_3H_6}$ = 4 atm, R = 2-PhInd, Al : Zr = 100. [m] Polymerisation was carried out in toluene, $p_{C_3H_6}$ = 4 atm, R = 2-PhInd, Al : Zr = 300. [n] Polymerisation was carried out in methylene chloride, $p_{C_3H_6}$ = 6 atm, Al : Zr = 480.

Analysis of the microstructure of the PP samples prepared with the **26** – MAO catalyst system led Naga and Mizunuma [100] to the conclusion that the formation of isotactic sequences during the growth of the polymer chain is dictated by the terminal unit ($4[mm][rr][mr]^{-2} \approx 1$) in the range of polymerisation temperatures of −20 to 40 °C. These results indicate that this stereocontrol mechanism may be involved in the propylene polymerisation under the action of 2-aryl-substituted metallocenes. The synthesis of the high-molecular-mass elSBPP on catalysts with C_2 symmetry,[101] namely, *rac*-$Me_2C(3\text{-}Pr^iInd)_2ZrCl_2$ and *rac*-$H_2C(3\text{-}Pr^iInd)_2ZrCl_2$, should also be mentioned. In the presence of MAO, at 50 °C in liquid propylene, these complexes (Al : Zr = 1000 – 4000) actively $\{A \approx 2.5$ kg PP (mmol Zr)$^{-1}$ $[C_3H_6]^{-1}$ $h^{-1}\}$ form amorphous polypropylene with a molecular mass of 100 000 – 160 000 g mol^{-1} and with a content of isotactic pentads of 15.6% for the former catalyst and 25.5% for the latter catalyst. The formation of stereo blocks on these catalysts is determined by the presence of two enantiomers with different isospecificity and a noticeable contribution of the stereocontrolling influence of the terminal unit of the polymer chain to the enantiomorphic stereocontrol. An increase in the reaction temperature is accompanied by a decrease in the content of isotactic pentads typical of metallocene complexes of C_2 symmetry (unlike catalysts of C_1 symmetry).[59, 61, 102]

An increase in the Al : Zr ratio accompanied by an increase in the activity of the **16** – MAO system reduces the content of isotactic pentads in the resulting polymer (see Table 3, rows 3, 7, 9). In this connection, it is of interest to turn to the data of Petoff *et al.*[103] Analysis of the effect of AlR_3 additives (R = Me, Bu^i) introduced in MAO demonstrated that aluminium alkyls decrease the activity of the *rac*- and, more appreciably, *meso*-form of $Me_2Si(2\text{-}PhInd)_2ZrCl_2$ but do not change substantially the microstructure of PP prepared on each complex alone. A pronounced increase in the polymer isotacticity upon the introduction of aluminium alkyls, accompanied by a decrease in the activity, was observed in the polymerisation guided by a mixture of *rac*- and *meso*-forms of the complex as the cationic *meso*-form became passive after coordination to TIBA. The addition of aluminium alkyls to the **16** – MAO system (Al_{MAO} : Zr = 1000) brought about a decrease in the activity by factors of 1.4 and 1.7 for R = Bu^i ($Al_{AlBu^i_3}$: Zr = 1000) and Me (Al_{AlMe_3} : Zr = 100), respectively, but induced an increase in the content of the *mmmm* pentads from 39% to 47% in the former case and a drop of this value to 19% in the latter case (similarly to polymerisation with a large excess of MAO). Thus, one cannot rule out the possibility of MAO participation in the stereocontrol through chain transfer between aspecific and isospecific sites by the $AlMe_3$ contained in MAO, as in the case of 'hybrid' metallocene catalysts considered below. Apparently, parameters of MAO (degree of oligomerisation, structural characteristics, Lewis acidity), which depend on the temperature and the presence and concentration of $AlMe_3$, are also important factors influencing the state of the active centre

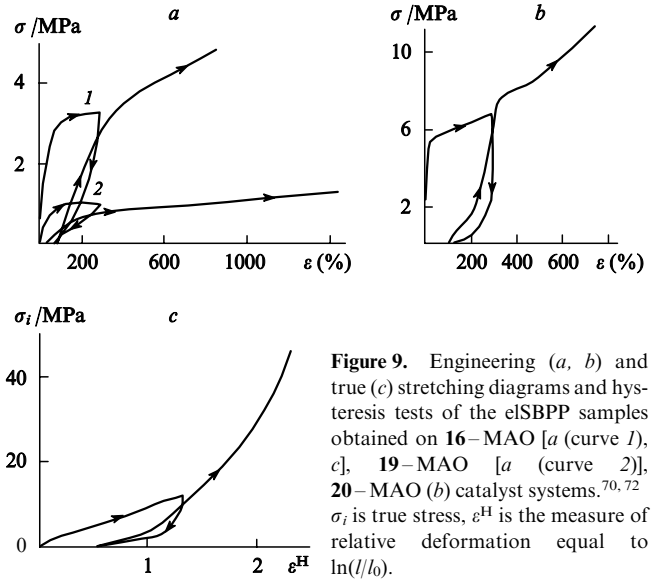


Figure 9. Engineering (*a, b*) and true (*c*) stretching diagrams and hysteresis tests of the elSBPP samples obtained on **16**–MAO [*a* (curve *1*), *c*], **19**–MAO [*a* (curve *2*)], **20**–MAO (*b*) catalyst systems.[70, 72] σ_i is true stress, ε^H is the measure of relative deformation equal to $\ln(l/l_0)$.

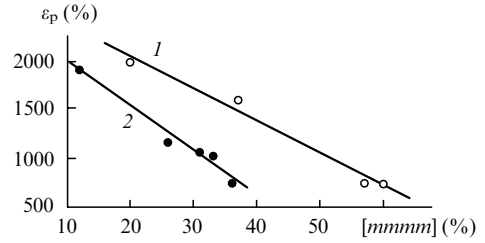


Figure 10. Elongation at rupture (ε_p) *vs.* content of isotactic pentads in elSBPP samples obtained on metallocenes of C_1 symmetry (*1*)[60] and 'oscillating' catalysts[72] (*2*).

(polarisation of the M–C bond, capacity for dissociation upon coordination and insertion of olefin).[104, 105]

The microstructure of stereoblock PP obtained in the presence of 'oscillating' catalysts differs from the microstructure of PP formed on catalysts with C_1 symmetry by a much higher content of heterotactic pentads, the average length of isotactic sequences being the same (see Table 5). It is also noteworthy that PP synthesised using 'oscillating' catalysts has a stereoblock structure even in samples with low contents of isotactic pentads. Thus a sample of elSBPP with good elastomeric properties formed on the **19**–MAO catalyst system contains only twice as many isotactic *mmmm* pentads as the ideal atactic PP and, correspondingly, half the syndiotactic *rrrr* pentads. In addition, the content of boundary *mmmr* pentads is higher, while that for *rrrm* is lower for stereoblock PP. The proportion of other pentads corresponds to atactic PP.

A lot of data on the strain, strength and elastomeric properties of elSBPP have now been accumulated.[70, 72, 80, 106–111] Figure 9 *a–c* shows the data on the relaxation dependences for stereoblock PP. It can be seen that polymer samples exhibit good elastomeric properties. The stretching curves follow a pattern typical of classical elastomers,[112] *i.e.*, they show uniform deformation upon stretching to great degrees of elongation and high reversibility of deformation.

Some properties of the elSBPP samples obtained on treatment with various types of catalyst are compared in Table 6. The elastomeric SBPP with macromolecules containing more uniform isotactic but also longer atactic sequences have higher melting temperatures but exhibit smaller elongation at rupture, while the molecular masses and the contents of the *mmmm* pentads are the same. Figure 10 illustrates the dependence of the elongation at rupture on the content of isotactic pentads for the PP samples prepared on metallocenes of various types. Figure 11 *a–c* presents the variation of the modulus of elasticity, tensile strength and the residual elongation *vs.* the molecular mass and the degree of crystallinity for the elSBPP samples synthesised in the presence of the metallocenes **16**, **19** and **20**. As can be seen from the data of Table 6 and Figs 10, 11, an increase in the molecular mass of polymers with invariant stereoregularity and degree of crystallinity results in a higher modulus of elasticity, tensile strength and a smaller residual elongation. A decrease in the stereoregularity for similar molecular masses and crystallinity degrees reduces the modulus of elasticity, the tensile strength and the residual elongation. An increase in the sample degree of crystallinity with invariant molecular masses and stereoregularity brings about an increase in the modulus of elasticity, the strength and the residual elongation. It can be seen that the strength and elastomeric properties are determined by several characteristics including the molecular mass, the degree of crystallinity and the stereoregularity of the polymer.

Presumably, the size and size distribution of the crystallites and the dynamic changes in the structure of the network junctions under the action of load at various temperatures are also signifi-

Table 6. Properties of the elSBPP prepared under the action of various metallocene catalyst systems.

Row	Catalyst	$10^{-3} M_w$ /g mol^{-1}	[*mmmm*] (%)	*C* (%)	T_p /°C	Elongation at rupture (%)	Tensile strength /MPa	Residual elongation (%) (see [a])	Ref.
1	**1**	127	40	7	51/66	525	4.0	57_{300}	51
2	**5**	30	38	7	47/61	200	3.0	–	56
3	**7**	49	54	19	54/93	500	16.0	90_{200} (see [c])	56
4	**7**	140	45	15	50/79	750	16.0	97_{200} (see [c])	58
5	**7**	380	52	17	53/74	800	39.0	93_{200} (see [c])	58
6	**10**	171	37	–	–	1700	6.0	–	60
7	**16**	160	31	4	140	1070	4.8	69_{300}	72
8	**16**	145	33	12	150	1015	6.8	101_{300}	72
9	**16**	410	26	3	141	1170	7.9	31_{300}	72
10	**20**	37	30	11	151	790	2.0	175_{300}	72
11	**20**	210	36	14	157	750	11.4	100_{300}	72
12	**20**	360	–	10	151	854	14.3	100_{300}	72
13	**19**	190	12	–	–	1930	1.5	47_{300}	72
14	**16**	455	32	11	138	878	9.3	$30–40_{300}$	79
15	**16** [b]	257	34	18	140	753	7.0	$50–90_{300}$	79

[a] The index shows the elongation (in %) after which the load was removed. [b] The sample was prepared in the presence of hydrogen. [c] Recovery.

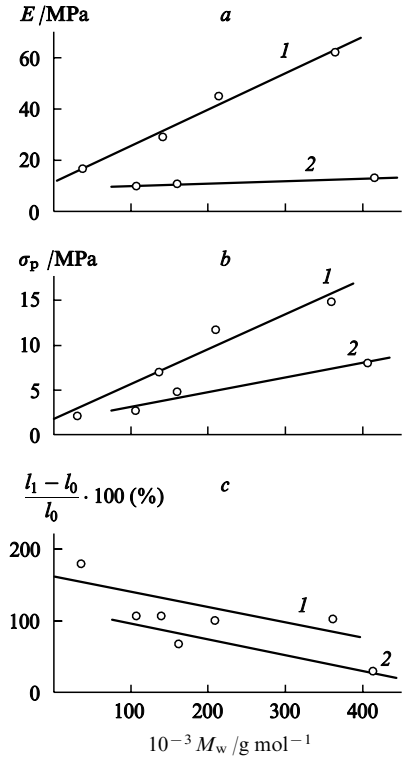


Figure 11. Modulus of elasticity, E (*a*), tensile strength, σ_p (*b*), and residual elongation, $(l_1-l_0)/l_0$ (*c*) *vs.* molecular mass of elSBPP samples with different degrees of crystallinity:[70, 72] (*1*) 10% – 14%, (*2*) 0% – 4%.

cant for strain and elastomeric parameters of elSBPP. However, at present, it is impossible to perform a comparative analysis of the effects of these factors on the mechanical properties of elSBPP samples obtained using different catalyst systems as no information needed for this purpose is available.

Thus, by varying the type of the catalyst or polymerisation conditions, one can prepare elSBPP possessing a required set of properties.

4. Catalyst systems based on metallocenes with activators other than polymethylaluminoxane

In the preceding sections, we considered metallocene catalysts for the synthesis of elastomeric PP activated by MAO. In these catalyst systems, MAO functions as an alkylating and a cation-generating reagent without being an effective controller of the microstructure or chain transfer agent.[80] The main factors that control the microstructure of the macromolecule in the catalyst systems considered above are the composition and structure of the initial catalyst and the monomer concentration. The catalyst systems containing MAO as a cocatalyst suffer from some drawbacks. The maximum activity of metallocene catalysts, in particular those considered in this review, is observed at great cocatalyst : catalyst ratios (see, for example, Table 3, rows 4 and 9). Due to the high cost of MAO, the catalysts are expensive. In this section, we give examples of metallocene catalyst systems in which other types of activating additives are used and also catalyst systems that provide additional possibilities of controlling the microstructure of the macromolecules formed.

a. The (2-PhInd)$_2$ZrMe$_2$ – TIBA catalyst systems

Recently, we found a new class of homogenous catalyst systems in which TIBA serves as the activating additive. In terms of activity in ethylene and propylene polymerisation, these catalysts are commensurable with systems containing MAO as the cocatalyst; they also retain the stereospecific action.[98, 113] This group of complexes includes the dimethyl derivatives of 2-substituted

Table 7. Polymerisation of propylene in toluene or in the liquid monomer induced by the (2-PhInd)$_2$ZrMe$_2$ – TIBA catalyst system.[98, 113]

Row	Al : Zr	$p_{C_3H_6}$ /atm	T_p /°C	A	[*mmmm*] (%)	D_{998}/D_{973}
1	120	see [a]	30	0.10	28	0.26
2	100	6.3	30	0.13	39	0.32
3	200	6.3	30	0.27	–	0.17
4	300	6.3	30	0.42	18	0.18
5	300	2.3	30	0.18	21	0.18
6	120	6.3	10	0.15	–	0.25
7	120	6.3	50	0.76	–	0.17

[a] Polymerisation was carried out in the liquid monomer; M_w = 230 000 g mol^{-1}, $M_w : M_n$ = 2.8.

bisindenyl zirconocenes, in particular, the dimethylated analogue of the complex **16**.

Study of the catalytic properties of the (2-PhInd)$_2$ZrMe$_2$ – TIBA system in toluene and in liquid monomer showed that its activity is similar to that of **16** – MAO, the molecular mass of the resulting elSBPP being the same or higher (Table 7). Unlike the **16** – MAO catalyst, for this system, no increase in the content of isotactic pentads following an increase in the monomer concentration was observed (see Table 7, rows 4, 5 and 1, 2). The concentration of TIBA or, with a constant metallocene concentration, the $Al_{TIBA} : Zr$ ratio is the factor which allows variation over broad ranges of the system activity, the kinetic characteristics of the polymerisation process and the properties of the PP formed. Thus an increase in the $Al_{TIBA} : Zr$ molar ratio from 100 to 300 entails a 4-fold increase in the activity, a growth of the molecular mass from 80 000 to 220 000 g mol^{-1} and a decrease in the content of isotactic pentads (Fig. 12). Yet another feature of this catalyst system is the fact that it permits polymerisation to be carried out at relatively high temperatures (see Table 7, row 7). The increase in the activity of the given system with an increase in the reaction temperature is not accompanied by a sharp decrease in the molecular mass, as was observed for the MAO-activated

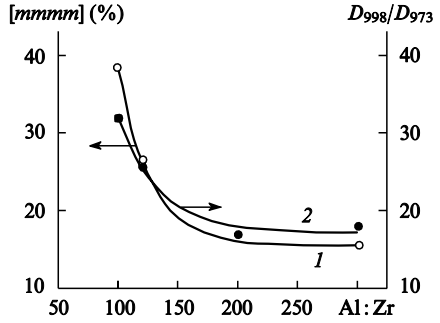


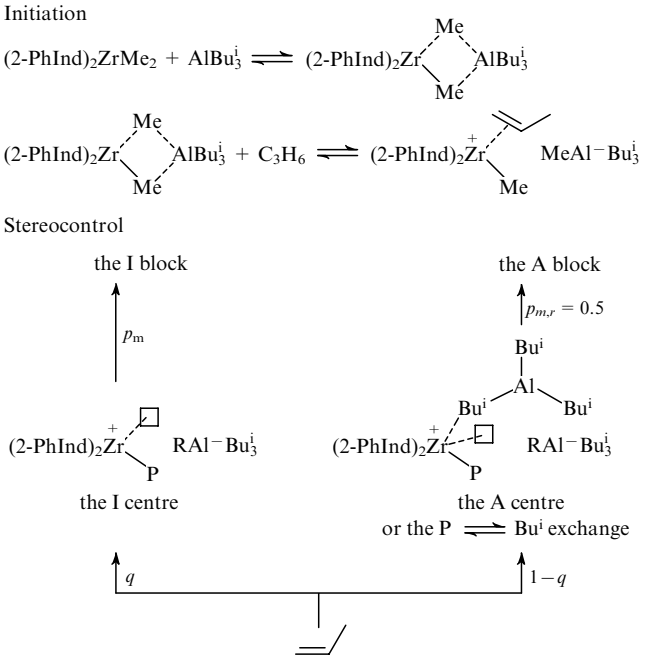
Figure 12. Pentad composition (*1*) and macrotacticity index (*2*) of elSBPP obtained with the (2-PhInd)$_2$ZrMe$_2$ – TIBA catalyst system *vs.* Al : Zr molar ratio (T_p = 30 °C).[113]

system, and makes it possible to change the isotacticity of elSBPP (see Table 7, rows 6, 7). Thus, by varying the concentration of the activating agent and the reaction temperature, one can prepare elSBPP with a specified set of properties.

Panin *et al.*[98] proposed a model which takes into account the participation of TIBA and the monomer in the formation of the AC (Scheme 3, initiation); this allows one to explain why the rate of polymerisation is first order with respect to TIBA and second order with respect to the monomer.

Another model explains the role of TIBA in the stereocontrolling action of the AC (Scheme 3, stereocontrol).[113] This model

Scheme 3



implies repeated inversion of the AC (fast dynamic equilibrium) from the isospecific to aspecific state during chain growth as a result of coordination of an additional TIBA molecule or the generation of 'errors' due to fast exchange between the alkyl groups of TIBA and the growing polymer chain.

Computer simulation of the growing chain of stereoblock PP ($\sim$300 000 units) was carried out with the optimised parameters of probability of monomer addition to the active site in the isospecific (q) or aspecific ($1-q$) state and the probability of monomer addition with a definite orientation in the isospecific centre (p_m). In all model experiments, the last-mentioned value was taken to be unity. The probability of *m*- or *r*-addition ($p_{m,r}$) in the aspecific AC was taken to be 0.5. The pentad composition of experimentally obtained elSBPP samples is consistent with the value calculated in terms of this model; in addition, a logical dependence of the q parameter on the TIBA concentration is observed.

It should be noted that elSBPP formed under the action of the $(2\text{-PhInd})_2ZrMe_2$–TIBA catalyst system is similar in pentad composition to the PP produced by the **16**–MAO system (see Table 5, 6) and exhibits similar elastomeric properties.

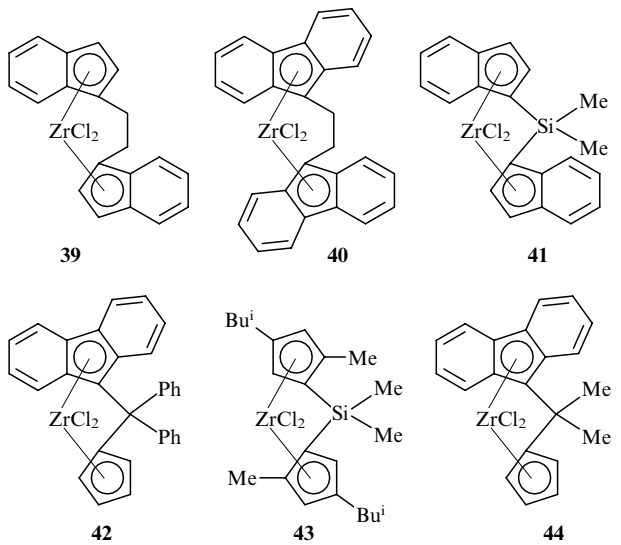
The attraction of this catalyst system for the synthesis of elSBPP is in the use of cheap trialkylaluminium instead of expensive MAO as the activating agent and in the possibility of changing the molecular-mass characteristics and the microstructure of the resulting polymer by varying the Al : Zr ratio and the polymerisation temperature. Apparently, the $(2\text{-PhInd})_2ZrMe_2$–TIBA system should be sensitive to the action of hydrogen and ethylene, like the **16**–MAO system described above.[79, 82, 85, 86] This provides additional opportunities for the control of activity, molecular mass and stereo and fractional composition of the polymer.

b. 'Hybrid' metallocene catalyst systems

The mechanisms of action of the above-described homogeneous metallocene catalyst systems for the synthesis of elSBPP have a common feature, *i.e.*, the possibility of the existence of a cationic AC in the isospecific or aspecific state. In recent years, publications appeared on the synthesis of stereoblock PP by polymerisation induced by mixtures of metallocenes with different stereospecificity, 'hybrid' homogeneous [114–116] or supported [117] catalyst systems.

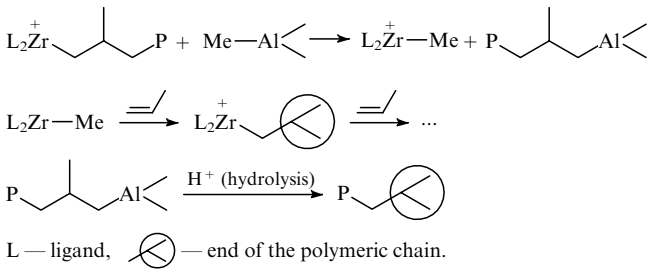
In studies on homogeneous catalyst systems, a combined activator for zirconocene dichlorides, namely, TIBA–$CPh_3B(C_6F_5)_4$ [114–116] or MAO [116] was used. Zirconocene dichlorides on a MAO-treated support were activated by TIBA.[117] Presumably, in the homogeneous system, TIBA acts as the alkylating agent in the initiation step, and the subsequent reaction of the alkylated catalyst with the borate gives rise to a cationic alkyl metal AC. The mechanism of activation of metallocene catalyst systems involving trialkylaluminium is currently open to question and its detailed discussion is beyond the scope of this review. Only some facts will be presented. Monoalkylation of a large series of zirconocene dichlorides induced by $AlMe_3$ has been confirmed experimentally.[118] In the case of the Cp_2ZrCl_2–TIBA system (Al : Zr = 10), a ^{13}C NMR study showed that the $Cp_2Zr(Bu^i)Cl\cdot TIBA$ complex is the only identifiable product (19%), whereas in the $(Me_5C_5)_2ZrCl_2$–TIBA system, the $(Me_5C_5)_2Zr^+Cl\cdots ClAl^-Bu^i_3$ complex is formed selectively.[119] Preliminary reaction of zirconocene dichlorides with MAO at relatively low Al : Zr ratios ($\sim 10^2$) results in complexes that are effectively activated by TIBA in the polymerisation of propylene.[120–122] The $Me_2Si(Me_4C_5)NBu^tZrCl_2$–MAO, $Me_2Si(Me_4C_5)NBu^tZrCl_2$–TIBA–$CPh_3B(C_6F_5)_4$ and $Me_2Si.(Me_4C_5)NBu^tZrMe_2$–TIBA–$CPh_3B(C_6F_5)_4$ systems exhibit different catalytic properties in ethylene polymerisation under identical conditions.[101, 123–125] Despite the fact that TIBA is widely used as an activator of immobilised metallocene complexes supported on MAO-treated materials,[126] no data on the mechanism of activation or the role of TIBA have been published. In a number of publications,[123, 127–130] it is noted that TIBA is not a chain transfer agent in homogeneous catalyst systems for ethylene and propylene polymerisation but functions as an activator.

Propylene polymerisation using a mixture of dichloride metallocene complexes with different stereospecificity, namely, isotactic–atactic complexes **39**–**40** or **41**–**40** [114] and isotactic–syndiotactic complexes **41**–**42** [115] activated by TIBA–$CPh_3B(C_6F_5)_4$ gave [114] high-molecular-mass products, which were mixtures of homopolymers with the composition corresponding to the stereospecific action of the initial catalysts and a stereoblock fraction. The catalyst systems studied by Chien *et al.*[114] exhibit activities of up to 50 kg PP (mol Zr)$^{-1}$ h^{-1} $[C_3H_6]^{-1}$. The content of the stereoblock fraction depends on the molar ratio of the complexes in the hybrid mixture and the TIBA concentration. The stereoblock fraction ensures the compatibility of the resulting polymers. An increase in the concentration of TIBA is accompanied by an increase in the activity of the systems and a decrease in the crystallinity of the polymeric product. At a definite composition, the resulting polymers exhibit good elastomeric properties: the elongation at rupture reaches 900% and the recovery is 97%–98%. The formation of the stereoblock fraction was attributed [114] to the fast exchange of growing polymeric chain

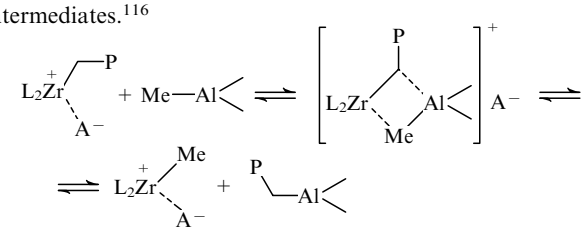


fragments between the AC with different stereospecificities with participation of TIBA.

Recently, experimental data have been published confirming the possible formation of the stereoblock PP fraction by the 'hybrid' mechanism.[116] Analysis of the terminal groups of the PP macromolecules formed under the action of zirconocenes with different structures, the isospecific complexes *rac*-Me_2Si.$(2\text{-MeInd})_2ZrCl_2$ (**45**) and **43**, the aspecific complex **40** and the syndiospecific zirconocene **42** activated by MAO or by the TIBA – $CPh_3B(C_6F_5)_4$ system showed that chain transfer to the organoaluminium compound proceeds efficiently for some catalysts. This is indicated by the high content of the isopropyl groups in the polymer.



The efficiency of chain transfer during propylene polymerisation on MAO (or $AlMe_3$ present in MAO) is governed by steric parameters of metallocene and is maximum for the sterically most hindered highly stereo- and regiospecific zirconocene **43**. The introduction of an additional amount of $AlMe_3$ (Al : Zr = 500 – 5000) results in a considerable increase in the activity and a decrease in the molecular mass of isotactic PP. The efficiency of the chain transfer to the organoaluminium compound reaches 95%; evidently, this process takes place through alkyl – polymer chain reversible exchange reactions in heteronuclear cationic intermediates.[116]



The aspecific complex **40** is less capable of chain transfer by this mechanism. The introduction of an additional amount of $AlMe_3$ results in a lower molecular mass of the polymer and a lower system activity, apparently, due to the formation of coordinatively saturated 'dormant' active centres.[131, 132] The chain transfer during polymerisation is less pronounced in the case of the syndiospecific complex **42** and does not take place when sterically open isospecific zirconocene **45** is used. On none of the zirconocenes studied, was transfer of the polymer chain to TIBA observed in the presence of a combined activator.

By combining complexes with different stereoselectivity (**40** – **43**) exhibiting the maximum capacity for chain transfer to the organoaluminium compound, it was possible to prepare PP with the highest (up to 30%) content of the stereoblock fraction (atactic – isotactic blocks) soluble in boiling hexane.[116] The proportion of the stereoblock fraction increases upon an increase in the content of the catalyst more prone to chain transfer to the organoaluminium compound.

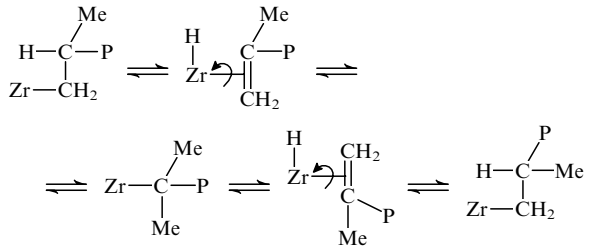
Unfortunately, the researchers cited[116] did not analyse the dependence of the content of the stereoblock fraction on the concentration of the complexes **40** and **43** and TIBA. A decrease in the concentrations of these components should decrease the probability of exchange reactions and thus reduce the amount of the stereoblock fraction. However, in a recent study,[133] doubt is cast upon the widely recognised opinion regarding the nature of the AC (the cationic metal alkyl site stabilised by the counter-ion). Analysis by NMR spectroscopy of anion exchange reactions (dynamic symmetrisation of ion pairs of zirconocene) which are accelerated in the presence of $Li^+\cdots MeB^-(C_6F_5)_3$ and upon an increase in the zirconocene concentration, mainly due to the entropy factor, provides grounds for belief that quadrupole ion – counter-ion dimers (or polynuclear complexes) act as AC for the ion-coordinate polymerisation of olefins. Proof of the existence of such intermediates would provide a new interpretation of exchange reactions involving zirconocenes with different stereospecificities.

Apparently, stereoblock PP is formed by a chain transfer mechanism between the AC with different specificity through TIBA or the monomer during propylene polymerisation induced by binary supported catalysts which have been reported recently.[117] These catalysts were synthesised by co-precipitation of the isospecific zirconocene **41** and the syndiospecific complex **44** from a toluene solution onto silica gel treated with MAO (PQ-SiO_2 – MAO). This method of deposition ensures homogeneous distribution of complexes on the surface of the support and creates the possibility for the arrangement of two AC possessing different stereospecific action in the close vicinity of each other. Comparison of the molecular-mass characteristics and the *xxxx*/*xxxy* ratios of the pentad contents (*x*, *y* = *m* or *r*) for the PP samples prepared on the PQ-SiO_2 – MAO – **41**, PQ-SiO_2 – MAO – **44** and PQ-SiO_2 – MAO – (**41** + **43**) catalyst systems with all other factors remaining the same showed that the polymer formed under the action of the binary supported catalyst contained a stereoblock fraction in addition to isotactic and syndiotactic fractions. On the basis of the analysis of ^{13}C NMR spectra, it was concluded[117] that the chain transfer to TIBA or to the monomer takes place, on average, after 75 steps of insertion. Apparently, due to the low activity of the catalyst and relatively low molecular mass of PP samples (40 000 – 50 000 g mol^{-1}), data on the properties of polymers are not presented in the publication. The melting temperatures of PP formed on the binary supported catalyst at 30 – 60 °C are close to those of IPP ([*mmmm*] ≈ 90%) prepared using the supported complex **41**. It should be noted that the use of 'hybridisation' with utilisation of procedures giving rise to highly effective immobilised catalysts[134] after optimisation of the conditions of their synthesis and polymerisation and with appropriate selection of metallocenes, can prove highly promising for the synthesis of elSBPP or polypropylene composites.

5. Catalyst systems of the post-metallocene type

Since the first publications[135, 136] and to the present day, the interest in the catalyst systems for olefin polymerisation based on chelates formed by Group VIII elements, so called post-metallocene catalyst systems, has continually increased. Most publications are devoted to the study of catalytic activity, the mechanisms of formation and the properties of polyethylene (PE) formed under the action of these systems (see, for example, reviews[137, 138]). In recent years, approaches to the design of chiral catalyst systems of this type effective for the synthesis of stereoregular PP have taken shape.[139 – 143] The chelate complexes of Group IVB metals can also be regarded as post-metallocene catalysts. In a number of publications,[144 – 146] high catalytic activity of these complexes activated by MAO in ethylene polymerisation has been reported. A number of publications have been devoted to the catalyst systems based on Group IVB metal chelate complexes efficient in the synthesis of elSBPP.[99, 147, 148]

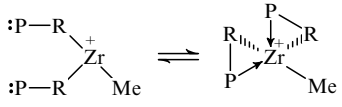
The catalytic activity of MAO-activated zirconium dichloride *rac*-bisacetylacetonate has been studied.[99] This catalyst system in toluene produces fractions of highly isotactic PP (76%) and elSBPP (24%), while in methylene chloride, elSBPP is formed as the only polymerisation product. It has been suggested[99] that the cationic metal alkyl complex with a coordinated toluene molecule exhibits an isospecific action. In methylene chloride, which is more polar than toluene, the electrophilicity of the cationic species is manifested as agostic interactions with the growing polymer chain, which result, however, in chain isomerisation rather than chain transfer.



Under certain conditions, this process competes with chain growth and acts a source of 'errors', which deteriorate the growth of isotactic sequences.

Unlike the mechanism realised on C_1-symmetric catalysts and giving rise to single *...mrrm...* stereodefects, this mechanism does not rule out the appearance of double 'errors' with the formation of short atactic sequences, which is indicated by the presence of intense signals corresponding to the *mrmm* + *rrmr*, *rmrm* and *rrrm* pentads in the ^{13}C NMR spectrum (see Table 5, row 25). An increase in the reaction temperature promotes more efficient isomerisation. To confirm the proposed mechanism, Shmulinson *et al.*[99] demonstrated that this system effectively catalyses isomerisation of oct-1-ene to oct-2-, -3- and -4-enes.

High-molecular-mass elastomeric SBPP (M_w = 120 000–160000 g mol^{-1}, $M_w : M_n$ = 1.7–2.4) is formed on chiral M(η^2-NPhPPh$_2$)$_2$(η^1-NPhPPh$_2$)$_2$ complexes (M = Ti, Zr) upon polymerisation in the liquid monomer at 25 °C.[147] Apparently, a reason for the formation of alternating isotactic–atactic sequences during polymerisation of propylene induced by these catalysts is reversible coordination of the phosphine ligand resulting in a dynamic equilibrium between the tetrahedral and octahedral isomers. The tetrahedral isomer is aspecific, while the octahedral one is isospecific. The ^{31}P NMR spectra recorded at room temperature point to the predominant formation of the octahedral isomer under the action of MAO, although the tetrahedral complex has also been identified.



the A centre the I centre

The dynamic equilibrium between the tetrahedral and octahedral isomers during polymerisation can result in the formation of isotactic and atactic sequences whose relative lengths are determined by the activity of the complexes. However, in the case of this catalyst system, this is not the only factor deteriorating the growth of isotactic sequences. As in the previous case, Kuhl *et al.*[147] observed isomerisation of alk-1-enes into internal olefins.

The possibility of formation of stereoblock PP as a result of the change in the AC geometry in a dynamic equilibrium during the growth of the polymer chain has been studied [148] in propylene polymerisation in the presence of Ti(III) and Ti(IV) bisallyl chelate complexes, [(Bu^{t}Me$_2$SiCH)$_2$CH]$_2$Ti(μ-Cl)$_2$Li·TMEDA (where TMEDA is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and [(Bu^{t}Me$_2$SiCH)$_2$CH]$_2$TiCl$_2$. Similar complexes of zirconium induce the formation of isotactic PP under the same conditions. Several allylic complexes of Group IVB metals active in olefin polymerisation have been described.[149–154] As a rule, these are half-sandwich zwitterion Ti(IV) and Zr(IV) complexes in which the allylic ligand stabilises the electronic state of the active site.[149–151] The allylic intermediates are described most often as products of deactivation (or temporary deactivation) of the AC.[152–154]

The Ti(III), Ti(IV) and Zr(III), Zr(IV) bisallylic complexes [148] present unusual examples of comprehensively characterised catalysts active in the polymerisation of ethylene and propylene, in which the M–allyl bond mimicks the type of binding in cene or chelating ligands, and the lability of the allylic bond (σ, η^1, η^3)[155–157] determines the stereocontrolling effect. An unusual finding is that paramagnetic bisallyl Zr(III) (μ_{eff} = 1.5 μ_B) and Ti(III) complexes (μ_{eff} = 1.7 μ_B) are active in the polymerisation of ethylene and propylene upon activation by a slight excess of MAO. Polymers formed in the presence of MAO-activated M(III) complexes possess the same properties as the polymers obtained with M(IV)–MAO catalyst systems (Table 8, rows 4, 5 and 10, 12). It was suggested that, under these conditions, the olefin undergoes oxidative addition to the M(III) bisallyl complex with subsequent formation of the cationic M(IV) alkyl AC upon treatment with MAO. However, participation of the monomer at the active centre initiation step is debatable because the specific activities of M(III)–MAO systems normalised to the monomer concentration are similar (see Table 8, rows 1, 2 and 4, 6).

Table 8. Polymerisation of propylene in toluene induced by the [(Bu^{t}Me$_2$SiCH)$_2$CH]$_2$M(μ-Cl)$_2$Li·TMEDA–MAO catalyst system, where M = Zr(III), Ti(III), and the [(Bu^{t}Me$_2$SiCH)$_2$CH]$_2$MCl$_2$–MAO catalyst system, where M = Zr(IV), Ti(IV).[148]

Row	Catalyst	Al : M	T_p /°C	$p_{C_3H_6}$ /atm	A	$10^{-3}M_w$ /g mol^{-1}	$M_w : M_n$ (%)	[*mmmm*]
1	Zr(III)	400	25	7.2	0.001	16	2.6	61
2	Zr(III)	800	25	7.2	0.003	16	5.3	56
3	Zr(III)	800	50	10.1	0.005	12	2.4	96
4	Zr(III)	1000	25	7.2	0.003	16	2.9	74
5	Zr(IV)	1000	25	7.2	0.002	15	2.9	71
6	Ti(III)	400	0	5.1	0.01	2030	3.6	33
7	Ti(III)	400	25	7.2	0.03	336	2.9	43
8	Ti(III)	400	50	10.1	0.04	78	5.5	45
9	Ti(III)	600	25	7.2	0.04	140	2.5	27
10	Ti(III)	1000	25	7.2	0.03	115	2.7	20
11	Ti(III)	1200	25	7.2	0.03	86	2.8	15
12	Ti(IV)	1000	25	7.2	0.03	115	2.7	22

These catalyst systems induce the formation of polyethylene with a very high molecular mass and a quite substantial polydispersity coefficient, especially in the case of zirconium complexes. Under the action of zirconium complexes, IPP is formed. An increase in the reaction temperature from 25 to 50 °C is accompanied by an increase in the isotacticity from 56% to 96% (see Table 8, rows 2, 3). Catalyst systems based on titanium complexes give rise to elSBPP. Ray *et al.*[148] believe that the dynamic change in the geometry of the AC, $C_{2v} \rightleftharpoons C_2$, caused by reversible $\eta^1 \rightleftharpoons \eta^3$ isomerisation of the allylic ligands is responsible for the formation of stereoblocks. Meanwhile, an increase in the Al/Ti ratio is accompanied by a decrease in the molecular mass of the polymer and the content of isotactic pentads and by some decrease in the system activity. Apparently, these facts indicate that the chain transfer by titanium complexes to the organoaluminium compound and the back reaction can account for the appearance of regular 'errors' in isotactic sequences, similar to the situation observed for the 'hybrid' catalyst systems. Unfortunately, the pentad composition of elSBPP prepared in the presence of Ti(III) and Ti(IV) bisallyl complexes was not reported in the study under discussion.[148]

III. Characteristic features of the structure of elastomeric stereoblock polypropylene and the nature of relaxation processes

The possibility of preparing elastomeric materials by homopolymerisation of propylene has triggered considerable interest in these processes. For many elastomers, the influence of the microstructure and the molecular-mass characteristics on the strain, elastic and thermal properties of polymers has been studied. A number of publications have been devoted to the investigation of the rates and mechanisms of the relaxation processes using

differential scanning calorimetry (DSC),[82, 110, 114] DSC performed in the quasi-isothermal stepwise mode,[158] dynamic mechanical analysis (DMA),[26, 158, 159] dynamic thermomechanical analysis (DMTA),[107] birefringence,[107] IR polarimetry [108] *etc*. The structure of the materials has been studied by X-ray diffraction analysis,[107] solid-phase ^{13}C NMR spectroscopy, scanning electron microscopy and atomic-force microscopy (AFM).[159] The elSBPP samples subjected to analyses were synthesised using different catalyst systems, both heterogeneous and homogeneous ones based on bridged and non-bridged metallocenes.

The materials prepared using heterogeneous catalysts, namely, non-modified TMC and supported catalysts based on tetraneophylzirconium have been studied.[110] The contents of the isotactic pentads in the PP were 60 mass % and 40 mass %, respectively. The samples studied had similar values of melt flow index (0.5 g min^{-1} at 230 °C under a load of 21.6 kg) and impact strength (280 – 300 kJ m^{-2}). The polymer prepared using TMC was characterised by a higher modulus of elasticity and tensile strength. The DSC curves for homopolymers exhibited clear-cut peaks for melting (from 155 to 140 °C), crystallisation (from 110 to 80°C) and glass transition (from 4 to −5 °C). The peaks observed at 50 °C correspond, evidently, to relaxation processes in the disordered phase. For the PP samples studied, the DMTA spectra were also measured; they indicated an increase in the material stiffness following an increase in the degree of isotacticity.

The DSC curves for compositionally homogeneous elSBPP samples completely soluble in ether (synthesised using *ansa*-metallocenes) display feebly pronounced melting and crystallisation peaks.[55, 57, 114]

In a study of the properties of elSBPP produced under the action of homogeneous systems based on non-bridged metallocenes, both the initial samples and separate fractions were analysed, first of all, the fraction soluble in boiling ether, the fraction soluble in boiling n-heptane and that insoluble in boiling n-heptane. For the polymer synthesised using the **16** – MAO catalyst system,[80] two melting peaks were detected (60 and 140 °C), whereas the ether-soluble fraction {36 mass %, [*mmmm*] = 0.19} showed no peaks in the DSC curves. In the case of the heptane-soluble fraction {43 mass %, [*mmmm*] = 0.33}, a broadened endothermic peak in the temperature range from 40 to 160 °C was found, pointing to broad size and stability distributions of the crystallites. According to ^{13}C NMR spectroscopy, all fractions had a stereoblock structure. For the fraction insoluble in n-heptane {57 mass %, [*mmmm*] = 0.38}, a melting peak at 150 °C is clearly defined. It can be seen from Fig. 13 that non-fractionated elSBPP exhibits small melting peaks. The pattern of the melting curves depends not only on the method used to prepare the samples but also on their thermal pre-history.

X-Ray diffraction analysis, DSC, and solid-phase ^{13}C NMR spectroscopy have been used to compare the structure of the crystallising and amorphous phases of non-fractionated samples and separate fractions of elSBPP prepared by polymerisation under different conditions and differing in the content of *mmmm* pentads and in the molecular mass.[107] Unlike the ether smectic fractions, fractions soluble and insoluble in n-heptane crystallise to give α- and γ-forms of PP. It is of interest that only formation of the α-form is noted for the initial polymer. To characterise the degree of ordering of amorphous phases, the influence of the temperature in the range of 20 – 80 °C on the peak intensity in the ^{13}C NMR spectra was studied. The content of the crystalline phase in the elSBPP samples determined from the ^{13}C NMR spectra in the solid phase is much higher than the values found by DSC or X-ray diffraction analysis. The results obtained attest to involvement of a synergistic effect in the crystallisation of polymers which contain easily crystallisable chains with high contents of isotactic sequences. The properties of polymers synthesised using the 'oscillating' catalyst and the catalyst containing *rac*- and *meso*-forms of *ansa*-zirconocene were compared as well as those of mixtures of isotactic and atactic PP. The materials were characterised by virtually equal contents of the *mmmm* pentads. The researchers noted [107] that the thermoplastic elastomers prepared by polymerisation, unlike blend compositions, possess excellent elastic properties even at elevated temperatures. In their opinion, the capacity for relaxation can be regarded as evidence for a multiblock structure of elSBPP. It has been shown by X-ray diffraction analysis, solid-phase NMR spectroscopy and birefringence that samples prepared in the presence of the **16** – MAO catalyst behave as elastomers up to a temperature of 80 °C at which they are subject to shear deformation, unlike mixtures of isotactic and atactic PP, which have similar stereoisomer compositions and degrees of crystallinity.

In order to gain a better understanding of the domain structure of elSBPP, Kravchenko *et al.*[158] studied the thermal and morphological properties of PP obtained using the **16** – MAO catalyst by the DSC method with temperature fractionation. The PP samples contained 25% and 30% isotactic *mmmm* pentad; their molecular masses were 240 000 – 260 000 g mol^{-1}. Preliminarily, the temperature of crystallisation for the studied samples varied from 160 to 50 °C with a step of 10 °C, and the samples were annealed at the appropriate temperatures for 12 h and then heated in the usual way. The resulting curves (Fig. 14) exhibit multiple peaks (Table 9) and differ substantially from the curves observed with fast scanning; this points to the influence of kinetic factors on the processes of crystallisation. Interesting results have been obtained by treating polymeric materials with hot nitric acid:[158] only ~10% of the polymer was insoluble (this corresponds to the content of perfect insoluble crystals). This method is widely used in the investigation of the structures of various polymeric materials. To characterise the domain structure of elSBPP samples, the AFM method was used.[158] Regions consisting of ribbon crystals distributed in the amorphous phase were found in the samples. It was also found [158] that the thickness of the lamellae in elSBPP equals 12 ± 4 nm, which corresponds to 54 monomer units. The elongation at rupture for the material

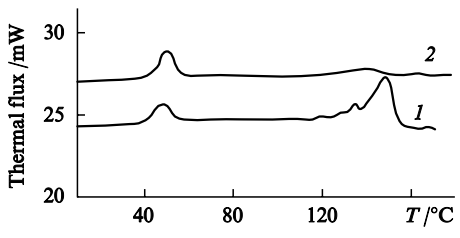


Figure 13. Comparison of the DSC curves of elSBPP samples (**16** – MAO catalyst system) with different contents of isotactic pentads.[80] (*1*) 30% (crystallinity, 11%), (*2*) 19% (crystallinity, 2%).

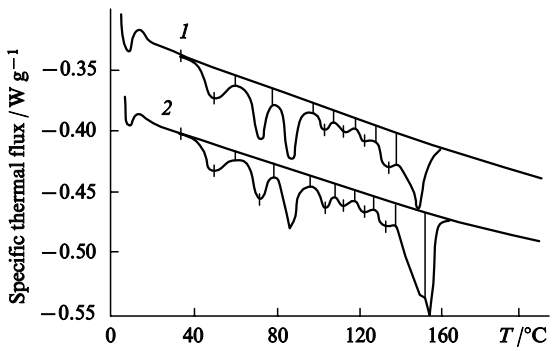


Figure 14. Temperature fractionation of DSC curves for two elSBPP samples with contents of isotactic *mmmm* pentads of 25% (*1*) and 30% (*2*).[158]

Table 9. Melting temperatures and heats for elSBPP samples subjected to stepwise annealing.[158]

[*mmmm*] (%)	T_m /°C	ΔH_m /J g^{-1}
25	46.32	1.059
25	68.71	2.242
25	83.19	3.091
25	100.12	1.274
25	109.11	0.938
25	119.34	0.963
25	129.72	1.399
25	150.07	5.520
25	151.63	2.210
		$\sum$ = 19.39 [a]
30	44.07	1.883
30	68.86	2.364
30	93.45	2.860
30	99.98	0.896
30	109.18	0.768
30	119.38	0.635
30	131.21	1.644
30	145.65	3.699
		$\sum$ = 14.93 [a]

[a] Total heat of melting.

studied reaches 1000% and the tensile strength was 15 MPa. When deformations do not exceed 300%, the hysteresis is high and no destruction of crystals in the samples is observed. In the case of great deformation, the initial lamellar crystallites are destroyed and small blocks are produced, which are mainly contained in fibrils. These processes are similar in mechanism to those taking place in other segmented elastomers such as aromatic polyesters and polyamides. The nanofibrils formed upon drawing contain alternant structures of rigid crystallites and, possibly, initially amorphous segments crystallising under the action of stress with chains oriented in the direction of drawing for both types of segments. The length of these domains is several hundreds of nanometers and the width is $\sim$12 nm. After relief of the stress and relaxation, the initial structure of the sample is not restored.

The results obtained in the studies of various samples of elSBPP and their fractions by DSC, DSC with temperature fractionation, by treatment with nitric acid and by AFM point to the cooperative nature of crystallisation processes and to the presence of diffusion and kinetic restrictions.

The rates of relaxation processes for compositionally inhomogeneous elSBPP and separate fractions have been studied by the birefringence method.[108] It was shown that the relaxation time and the size of the relaxation plateau depend on the temperature and shear deformation. In the case of 100% deformation, the relaxation time decreases as the temperature rises (2 h at 25 °C, 900 s at 80 °C, and 440 s at 115 °C), and the size of the relaxation plateau changes from 0.62 at 25 °C to 0.43 at 85 °C.[107] The effect of temperature on the rate of the relaxation processes for non-fractionated samples and for separate fractions of PP at different shear deformations (3% to 100%) was studied in detail. In the temperature range of 200 – 105 °C, complete isotropisation occurs rapidly. At 105 °C and at lower temperatures, the rates and the degrees of isotropisation for the initial samples and for separate fractions are markedly different. It is of interest that repeated application of shear strain resulted under some conditions in an increase in the rate and the degree of relaxation.

The results of studies [107, 110] indicate that great shear deformations ($\geqslant$50%) are able to destroy the physical junctions at weak points; this gives smaller crystals. An increase in the deformation results in irreversible anisotropy of non-equilibrium crystals. The fractions insoluble in heptane exhibit properties typical of solid elastomers; they are able to induce co-crystallisation of fractions with lower isotacticity. This results in a higher cross-linking density. It was concluded that the composition and the cooperative role of different fractions determine the elastic properties of materials.

Madkour and Mark [111, 160] arrived at analogous conclusions. The effect of the molecular mass, MMD and the length and length distribution of isotactic blocks on the moduli of elasticity of the materials have been studied by mathematical modelling. Modelling with allowance for co-crystallisation processes gave the dependences of the modulus of elasticity on the content of isotactic sequences similar to those established experimentally.

The results of an investigation of the fracture mechanism and examination of the fracture surface of elSBPP by scanning electron microscopy are rather interesting.[110] The dependence of the fracture energy on the stereochemical composition was elucidated. When the content of the *mmmm* pentads decreases from 60% to 40%, the cohesion energy of fracture for the samples studied changes from 8 to 20.6 kJ m^{-2}, and the plastic energy, from 53.8 to 9.4 kJ m^{-2}. In the examination of the fracture surface, the formation of sinusoidal structures parallel to the sample surface and tto he load axis has been observed for some samples (Fig. 15). Structures of this type have been described only for some thermoplastic elastomers.

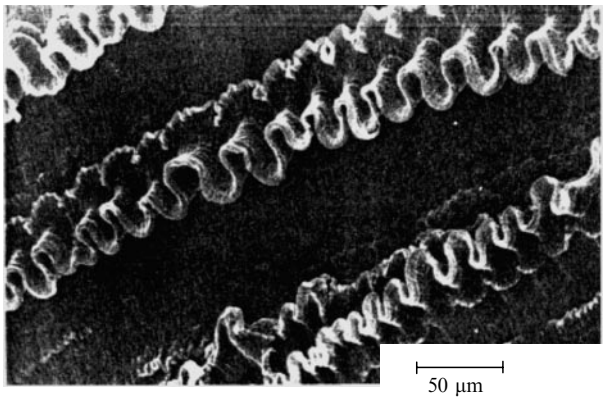


Figure 15. Photomicrograph of the fracture surface of the elSBPP sample.[110]

Thus, it was shown that the regularities observed for elSBPP are similar to those typical of crystalline elastomeric materials. The structure and the properties of the elastomeric PP, as well as of a number of other elastomers are due to the formation of crystallites from thin lamellae or nanofibrils joined by straightened or bent transient chains, which form an amorphous phase in addition to the end chains. The number, volume and the structure of junctions in the physical networks and the degree of ordering of the amorphous phase, the surface free energy of lamellae (end faces), and the values of cohesion and plastic energy determine the sub- and microstructure, the elastomeric properties of these materials, and the patterns of the observed dependences.

IV. Conclusion

The information considered above shows that the discovery of highly effective homogeneous metallocene and post-metallocene catalyst systems has stimulated work on the synthesis of new materials based on polyolefins. Among these, thermoplastic elastomeric stereoblock PP occupies a special place. The interest in its synthesis is great because these polymers can be used as adhesives, binders or elastic films. Numerous catalyst systems and their mixtures have been developed, which allow targeted control of the microstructure and molecular-mass characteristics of elastomeric stereoblock polymers. The mechanism of catalytic

and stereospecific action of these catalysts has been studied. Data on the influence of the microstructure on the mechanical, thermal and relaxation properties of elastomers have been obtained.

This review surveys the state-of-the-art of the research along this line. The necessity of this generalisation is dictated by the vigorous development of the work dealing with the design of new polymeric and structural materials.

This review was financially supported by the Russian Foundation for Basic Research (Projects No. 99-03-32948a and No. 01-03-97002 — regional, Moscow region).

References

1. L L Bohm, J Berthold, H-F Enderle, M Fleissner, in *Metalorganic Catalysts for Synthesis and Polymerisation: Recent Results by Ziegler–Natta and Metallocene Investigations* (Ed. W Kaminsky) (Berlin: Springer, 1999) p. 3
2. P Galli, G Ceccin, J C Chadwick, D Del Duca, G Vecellio, in *Metalorganic Catalysts for Synthesis and Polymerisation: Recent Results by Ziegler–Natta and Metallocene Investigations* (Ed. W Kaminsky) (Berlin: Springer, 1999) p. 14
3. P Galli, G Vecellio, in *Organometallic Catalysts and Olefin Polymerization. Catalysts for a New Millennium* (Eds R Blom, A Follestad, E Rytter, M Tilset, M Ystenes) (Berlin: Springer, 2001) p. 169
4. *Polypropylene. Past, Present and Future: The Challenge Continues* (Ferrara: Montell, 1998)
5. D A Walker, J D McCullough, F D Hussein *ANTEC'89* 851 1989
6. G Penzo, in *Polypropylene. Past, Present and Future: The Challenge Continues* (Ferrara: Montell, 1998) p. 53
7. G D Bukatov, V S Goncharov, V A Zakharov *Macromol. Chem. Phys.* **196** 1751 (1995)
8. U Zucchini, T Dell'Occo, L Resconi *Indian J. Technol.* **31** 247 (1993)
9. A L Rice, D R Parikh, J J Gathers, in *Proceedings of MetCon'99 'Polymer in Transition', Houston, TX, 1999*
10. E Albizzati, U Giannini, G Morini, M Galimberti, L Barino, R Scordamaglia *Macromol. Symp.* **89** 73 (1995)
11. V A Zakharov, L G Echevskaya, G D Bukatov *Polimery* **34** 277 (1989)
12. G Fink, R Mülhaupt, H H Brintzinger (Eds) *Ziegler Catalysts. Recent Innovations and Technological Improvements* (Berlin: Springer, 1995)
13. H-H Brintzinger, D Fischer, R Mülhaupt, B Rieger, R Waymouth *Angew. Chem., Int. Ed. Engl.* **34** 1143 (1995)
14. K Mashima, Y Nakayama, A Nakamura *Adv. Polym. Sci.* **133** 1 (1997)
15. W Kaminsky *J. Chem. Soc., Dalton Trans.* **9** 1413 (1998)
16. *J. Mol. Catal. A, Chem.* **128** (Spec. Issue) (1998)
17. W Kaminsky (Ed.) *Metalorganic Catalysts for Synthesis and Polymerisation: Recent Results by Ziegler–Natta and Metallocene Investigations* (Berlin: Springer, 1999)
18. *Top. Catal.* **7** (Spec. Issue) (1999)
19. *Chem. Rev.* **100** (Spec. Issue) (2000)
20. R Blom, A Follestad, E Rytter, M Tilset, M Ystenes (Eds) *Organometallic Catalysts and Olefin Polymerization. Catalysts for a New Millennium* (Berlin: Springer, 2001)
21. W Kaminsky, M Arndt *Adv. Polym. Sci.* **127** 143 (1997)
22. B A Krenstel, Y V Kissin, V I Kleiner, L L Stotskaya *Polymers and Copolymers of Higher Olefins* (Munich; Vienna; New York: Carl Hanser Verlag, 1997)
23. V T Ponomareva, N N Likhacheva *Plast. Massy* **4** 8 (2001)
24. V I Tsvetkova *Vysokomol. Soedin., Ser. C* **42** 1954 (2000) [a]
25. US P. 6 184 327 (2001)
26. US P. 6 265 512 (2001)
27. F S Dyachkovskii, V I Tsvetkova *Kinet. Katal.* **35** 534 (1994) [b]
28. F S Dyachkovskii, A K Shilova, A E Shilov *J. Polym. Sci., Part C, Polym. Symp.* **16** 2333 (1967)
29. Y V Kissin *Isospecific Polymerization of Olefins* (New York: Springer, 1985)
30. E I Vizen, L A Rishina, L N Sosnovskaya *Kinet. Katal.* **35** 743 (1994) [b]
31. A Zambelli P Lokatelli, M C Sacchi, E Rigamonti *Macromolecules* **13** 798 (1980)
32. M C Sacchi, E Barsties, I Tritto, P Locatelli, H-H Brintzinger, U Stehling *Macromolecules* **30** 1267 (1997)
33. L Cavallo, G Guerra P Corradini *J. Am. Chem. Soc.* **120** 2428 (1998)
34. F A Bovey, G V D Tiers *J. Polym. Sci.* **44** 173 (1960)
35. F A Bovey *Chain Structure and Conformation of Macromolecules* Ch. 3 (New York: Academic Press, 1982)
36. A Zambelli, P Locatelli, A Provasoli, D R Ferro *Macromolecules* **13** 267 (1980)
37. J A Ewen *J. Am. Chem. Soc.* **106** 6355 (1984)
38. V Busico, R Cipullo, G Monaco, M Vacatello, A L Segre *Macromolecules* **30** 6251 (1997)
39. I Pasquon *Pure Appl. Chem.* **15** 465 (1967)
40. W Kaminsky, K Kulper, H Brintzinger, F Wild *Angew. Chem., Int. Ed. Engl.* **24** 507 (1985)
41. J A Ewen, R L Jones, A J Razavi *J. Am. Chem. Soc.* **110** 6255 (1988)
42. J A Ewen *J. Mol. Catal. A., Chem.* **128** 103 (1998)
43. G Natta, G Mazzanti, G Crespi, G Moraglio *Chim. Ind. (Milan)* **39** 275 (1957)
44. US P. 3 175 999 (1965)
45. US P. 4 335 225 (1982)
46. J W Collette, C W Tullock, R N MacDonald, W H Buck, A C L Su, J R Harell, R Mulhaupt, B C Anderson *Macromolecules* **22** 3851 (1989)
47. J W Collette, D W Overnall, W H Buck, R C Ferguson *Macromolecules* **22** 3858 (1989)
48. US P. 5 270 410 (1993)
49. V I Tsvetkova, D M Lisitsyn, B A Uvarov, L A Novokshonova, L A Rishina *Stereospetsificheskaya Polimerizatsiya Propilena (Preprint)* [Stereospecific Polymerisation of Propylene (Preprint)] (Chernogolovka: Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, 1983)
50. USSR P. 682 262; *Byull. Izobret.* (32) 27 (1979)
51. D T Mallin, M D Raush, J C W Chien *J. Am. Chem. Soc.* **112** 2030 (1990)
52. J C W Chien, in *Ziegler Catalyst* (Eds G Fink, R Mülhaupt, H H Brintzinger) (Berlin: Springer, 1995) p. 200
53. H N Cheng, G N Babu, R A Newmark, J C W Chien *Macromolecules* **25** 6980 (1992)
54. G N Babu, H N Cheng, G H Llinas, J C W Chien *Macromolecules* **25** 7400 (1992)
55. US P. 575 6614 (1998)
56. W J Gauthier, S Collins *Macromol. Symp.* **98** 223 (1995)
57. W J Gauthier, S Collins *Macromolecules* **28** 3771 (1995)
58. W J Gauthier, S Collins *Macromolecules* **28** 3779 (1995)
59. U Dietrich, M Hackmann, B Rieger, M Klinga, M Leskelä *J. Am. Chem. Soc.* **121** 4348 (1999)
60. B D Coleman, T G Fox *J. Chem. Phys.* **38** 1065 (1963)
61. J Kukral, P Lehmus, T Feifel, C Troll, B Rieger *Organometallics* **19** 3767 (2000)
62. M K Leclerc, H H Brintzinger *J. Am. Chem. Soc.* **118** 9024 (1996)
63. V Busico, L Caporaso, R Cipullo, L Landriani, G Angelini, A Margonelli, A L Segre *J. Am. Chem. Soc.* **18** 2105 (1996)
64. V Busico, R Cipullo, L Caporaso, G Angelini, A L Segre *J. Mol. Catal. A, Chem.* **128** 53 (1998)
65. L Resconi *J. Mol. Catal. A, Chem.* **146** 167 (1999)
66. L Resconi, L Cavallo, A Fait, F Piemontesi *Chem. Rev.* **100** 1253 (2000)
67. G W Coates, R M Waymouth *Science* **267** 217 (1995)
68. E Hauptmann, R M Waymouth, J W Ziller *J. Am. Chem. Soc.* **117** 11586 (1995)
69. US P. 5 594 080 (1997)
70. V I Tsvetkova, P M Nedorezova, N M Bravaya, D V Savinov, I L Dubnikova, V A Optov *Vysokomol. Soedin., Ser. A* **39** 389 (1997) [a]
71. R Kravchenko, A Masood, R M Waymouth, C L Myers *J. Am. Chem. Soc.* **120** 2039 (1998)
72. P M Nedorezova, V I Tsvetkova, N M Bravaya, D V Savinov, V A Optov *Vysokomol. Soedin., Ser. A* **42** 901 (2000) [a]
73. M D Bruce, G W Coates, E Hauptmann, R M Waymouth, J W Ziller *J. Am. Chem. Soc.* **119** 11174 (1997)

74. O N Babkina, T A Bazhenova, N M Bravaya, V V Strelets, M Yu Antipin, K A Lysenko *Izv. Akad. Nauk, Ser. Khim.* 1529 (1996) [c]
75. T A Bazhenova, M Yu Antipin, O N Babkina, N M Bravaya, K A Lysenko, V V Strelets *Izv. Akad. Nauk, Ser. Khim.* 2161 (1997) [c]
76. P Witte, T K Lal, R M Waymouth *Organometallics* **18** 4147 (1999)
77. J L M Petoff, M D Bruce, R M Waymouth, A Masood, T K Lal, R W Quan, S J Behrend *Organometallics* **16** 5909 (1997)
78. S Lin, E Hauptman, T K Lal, R M Waymouth, R W Quan, A B Ernst *J. Mol. Catal. A, Chem.* **136** 23 (1998)
79. R Kravchenko, R M Waymouth *Macromolecules* **31** 1 (1998)
80. S Lin, C D Tagge, R M Waymouth, M Nele, S Collins, J C Pinto *J. Am. Chem. Soc.* **122** 11275 (2000)
81. G Y Lee, M Xue, M S Kang, O C Kwon, J-S Yoon, Y-S Lee, H S Kim, H Lee, I-M Lee *J. Organomet. Chem.* **558** 11 (1998)
82. Y Hu, M T Krejchi, C D Shan, C L Myers, R M Waymouth *Macromolecules* **31** 6908 (1998)
83. M Kakugo, T Miyatake, Y Naito, K Mizunuma *Macromolecules* **21** 314 (1988)
84. R Kravchenko, A Masood, R M Waymouth *Organometallics* **16** 3635 (1997)
85. C D Tagge, R L Kravchenko, T K Lal, R M Waymouth *Organometallics* **18** 380 (1999)
86. S Lin, R Kravchenko, R M Waymouth *J. Mol. Catal. A, Chem.* **158** 423 (2000)
87. S Lin, R M Waymouth *Macromolecules* **32** 8283 (1999)
88. J Petoff, T Ageston, T Lai, R Waymouth *J. Am. Chem. Soc.* **120** 11316 (1998)
89. M D Bruce, R M Waymouth *Macromolecules* **31** 2707 (1998)
90. M Nele, S Collins, M L Dias, J C Pinto, S Lin, R M Waymouth *Macromolecules* **33** 7249 (2000)
91. V Busico, D Brita, L Caporaso, R Cipullo, M Vacatello *Macromolecules* **30** 3971 (1997)
92. L Cavallo, G Guerra P Corradini *Gaz. Chim. Ital.* **126** 463 (1996)
93. M A Pietch, A K Rappé *J. Am. Chem. Soc.* **118** 10908 (1996)
94. N Schneider, F Schaper, K Schmidt, R Kirsten, A Geyer, H H Brintzinger *Organometallics* **19** 3597 (2000)
95. J C Randall *Polymer Sequence Determination: Carbon 13 NMR Method* (New York: Academic Press, 1977)
96. J-S Yoon, Y-S Lee, E-S Park, I-M Lee, D-K Park, S-O Jung *Eur. Polym. J.* **36** 1271 (2000)
97. T Dreier, G Erker, R Fröhlich, B Wibbeling *Organometallics* **19** 4095 (2000)
98. A N Panin, Z M Dzhabieva P M Nedorezova, V I Tsvetkova, S L Saratovskikh, O N Babkina, N M Bravaya *J. Polym. Sci., Part A, Polym. Chem.* **39** 1915 (2001)
99. M Shmulinson, M Galan-Fereres, A Lisovskii, E Nelkenbaum, R Semiat, M S Eisen *Organometallics* **19** 1208 (2000)
100. N Naga, K Mizunuma *Polymer* 2703 (1998)
101. D Baldoni, G Moscardi, G Baruzzi, V Braga, I Camurati, F Piemontesi, L Resconi, I E Nifant'ev, V Venditto, S Antinucci *Macromol. Chem. Phys.* **202** 1780 (2001)
102. E J Thomas, J C W Chein, M D Rausch *Macromolecules* **33** 1546 (2000)
103. J L M Petoff, C L Myers, R M Waymouth *Macromolecules* **32** 7984 (1999)
104. V A Zakharov, E P Talzi, I I Zakharov *Kinet. Katal.* **40** 926 (1999) [b]
105. D E Babushkin, Candidate Thesis in Chemical Sciences, Institute of Catalysis, Siberian Branch of Russian Academy of Sciences, Novosibirsk, 1999
106. E D Carlson, M T Krejchi, C D Shan, T Terekawa, R M Waymouth, G G Fuller *Macromolecules* **31** 5343 (1998)
107. Y Hu, E D Carlson, G G Fuller, R M Waymouth *Macromolecules* **32** 3334 (1999)
108. E D Carlson, G G Fuller, R M Waymouth *Macromolecules* **32** 8094 (1999)
109. E D Carlson, G G Fuller, R M Waymouth *Macromolecules* **32** 8100 (1999)
110. D E Mouzakis, M Gahleitner, J Karger-Kocsis *J. Appl. Polym. Sci.* **70** 873 (1998)
111. T M Madkour, J E Mark *Polymer* **39** 6085 (1998)
112. Yu K Godovskii, in *Trudy 4-i Sessii 'Inzhenerno-Khimicheskaya Nauka dlya Peredovykh Tekhnologii', Moskva, 1998* (Proceedings of the Fourth Session 'Engineering Chemical Science for Advanced Technologies', Moscow, 1998 p. 115
113. O N Babkina, N M Bravaya, P M Nedorezova, S L Saratovskikh, V I Tsvetkova *Kinet. Katal.* **43** (2002) (in the press) [b]
114. J C W Chien, Y Iwamoto, M D Rausch, W Wedler, H H Winter *Macromolecules* **30** 3447 (1997)
115. J C W Chien, Y Iwamoto, M D Rausch *J. Polym. Sci., Part A, Polym. Chem.* **37** 2439 (1999)
116. S Lieber, H-H Brintzinger *Macromolecules* **33** 9192 (2000)
117. C Przybyla, G Fink *Acta Polym.* **50** 77 (1999)
118. S Beck, H H Brintzinger *Inorg. Chim. Acta* **270** 376 (1998)
119. I Tritto, D Zucchi, M Destro, M C Sacchi, T Dall'Occo, M Galimberti *J. Mol. Catal. A, Chem.* **160** 107 (2000)
120. O M Khukanova, O N Babkina, L A Rishina P M Nedorezova, N M Bravaya *Polimery* **45** 328 (2000)
121. P M Nedorezova, V I Tsvetkova, A M Aladyshev, D V Savinov, I L Dubnikova, V A Optov, D A Lemenovskii *Polimery* **45** 333 (2000)
122. P M Nedorezova, V I Tsvetkova, A M Aladyshev, D V Savinov, A N Klyamkina, V A Optov, D A Lemenovskii *Vysokomol. Soedin., Ser. A* **43** 605 (2001) [a]
123. N M Bravaya, A N Panin, O N Babkina, N D Karpova *Polimery* **46** 397 (2001)
124. A N Panin, T A Sukhova, N M Bravaya *J. Polym. Sci., Part A, Polym. Chem.* **39** 1901 (2001)
125. A N Panin, I L Dubnikova, N M Bravaya *Izv. Akad. Nauk, Ser. Khim.* 1189 (2000) [c]
126. G G Hlatky *Chem. Rev.* **100** 1347 (2000)
127. R Kleinschmidt, Y Leek, M Reffke, G Fink *J. Mol. Catal. A, Chem.* **148** 29 (1999)
128. G Luft, R A Dyroff, C Gltz, S Schmitz, T Wieczorek, R Klimesch, A Gonioukh, in *Metalorganic Catalysts for Synthesis and Polymerisation: Recent Results by Ziegler – Natta and Metallocene Investigations* (Ed. W Kaminsky) (Berlin: Springer, 1999) p. 651
129. I Kim, J M Choi *J. Polym. Sci., Part A, Polym. Chem.* **37** 1523 (1999)
130. I Kim, J M Zhou *J. Polym. Sci., Part A, Polym. Chem.* **37** 2093 (1999)
131. M Bochmann, S Lancaster *Angew. Chem., Int. Ed. Engl.* **33** 1634 (1994)
132. K Vanka, T Ziegler *Organometallics* **20** 905 (2001)
133. S Beck, S Lieber, F Schaper, A Geyer, H-H Brintzinger *J. Am. Chem. Soc.* **123** 1483 (2001)
134. D Harrison, I M Coulter, S Wang, S Nistala, B A Kuntz, M Pigeon, J Tian, S Collins *J. Mol. Catal. A, Chem.* **128** 65 (1998)
135. L K Johnson, C M Killian, M S Brookhart *J. Am. Chem. Soc.* **117** 6414 (1995)
136. C M Killian, D J Tempel, L K Johnson, M Brookhart *J. Am. Chem. Soc.* **118** 11664 (1996)
137. G J P Britovsek, V C Gibson, D F Wass *Angew. Chem., Int. Ed.* **38** 428 (1999)
138. S D Ittel, L K Johnson, M Brookhart *Chem. Rev.* **100** 1169 (2000)
139. C Pellecchia, A Zambelli *Macromol. Rapid Commun.* **17** 333 (1996)
140. C Pellecchia, A Zambelli, L Oliva, D Pappalardo *Macromolecules* **29** 6990 (1996)
141. C Pellecchia, A Zambelli, M Mazzeo, D Pappalardo *J. Mol. Catal. A, Chem.* **128** 229 (1998)
142. B L Small, M Brookhart *Macromolecules* **32** 2120 (1999)
143. E F McCord, S J McLain, L T J Nelson, S D Arthur, E B Coughlin, S D Ittel, L K Johnson, D Tempel, C M Killian, M Brookhart *Macromolecules* **34** 362 (2001)
144. T Fujita, M Mitani, Y Tohi, H Makio, N Kihara, in *Proceedings of MetCon'99 'Polymer in Transition',. Houston, TX, 1999*
145. C Wang, S Friedrich, T R Younkin, R T Li, R H Grubbs, D A Bansleben, M W Day *Organometallics* **17** 3149 (1998)
146. T R Younkin, E F Connor, J I Henderson, S K Friedrich, R H Grubbs, D A Bansleben *Science* **287** 460 (2000)
147. O Kuhl, T Koch, F B Somoza P C Junk, E Hey-Hawkins, D Plat, M S Eisen *J. Organomet. Chem.* **604** 116 (2000)
148. B Ray, T G Neyroud, M Kapon, Y Eichen, M S Eisen *Organometallics* **20** 3044 (2001)

149. M Bochmann *Top. Catal.* **7** 9 (1999)
150. G Erker *Acc. Chem. Res.* **34** 309 (2001)
151. B Hessen, H van der Heijden *J. Organomet. Chem.* **534** 237 (1997)
152. L Resconi, I Camurati, O Sudmeijer *Top. Catal.* **7** 145 (1999)
153. G Moscardi, L Resconi, L Cavollo *Organometallics* **20** 1918 (2001)
154. V K Dioumaev, J F Harrod *Organometallics* **16** 1452 (1997)
155. G Erker, K Berg, K Angermund, C Krüger *Organometallics* **6** 2620 **(**1987)
156. M B Abrams, J C Yoder, C Loeber, M W Day, J E Bercaw *Organometallics* **18** 1389 (1999)
157. J Karl, M Dahlmann, G Erker, K Bergander *J. Am. Chem. Soc.* **120** 5643 (1998)
158. R L Kravchenko, B B Sauer, R Scott McLean, M Y Keating, P M Cotts, Y H Kim *Macromolecules* **33** 11 (2000)
159. E E Al'yanova, N M Bravaya, T I Ponomareva, V I Tsvetkova, P M Nedorezova, V I Irzhak *Vysokomol. Soedin., Ser. B* **40** 1691 (1998) [a]
160. T M Madkour, J E Mark *Polym. Bull.* **39** 385 (1997)

[a] — *Polym. Sci. (Engl. Transl.)*
[b] — *Kinet. Catal. (Engl. Transl.)*
[c] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*