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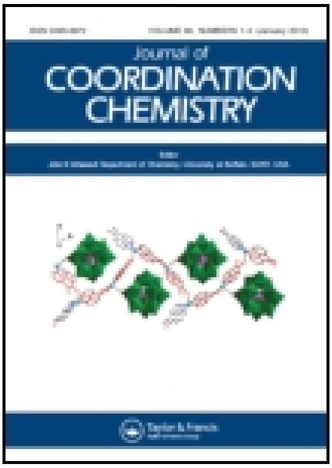

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Preparation method of superactive Ziegler-Natta catalysts to produce ultra-high molecular weight amorphous poly(1-octene), poly(1-decene), and their copolymers

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Preparation method of superactive Ziegler–Natta catalysts to produce ultra-high molecular weight amorphous poly(1-octene), poly(1-decene), and their copolymers

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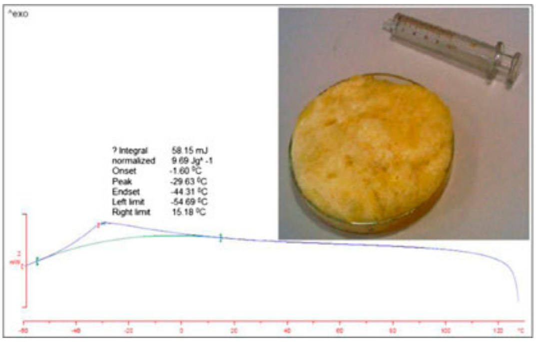

In this article, highly active and long-term stable Ziegler–Natta catalysts were formulated. 1-Octene and 1-decene homopolymerization and copolymerization were carried out with the prepared catalysts and the effect of catalyst formulation on the molecular weight and crystallinity level of polymers were investigated. Also, the valence state of Ti species was determined using X-ray photoelectron spectroscopy. The polymer molecular weights were determined by measuring the intrinsic viscosity. T_C and degree of crystallinity were obtained from the second heating curve of differential scanning calorimetry analysis. Using these catalysts, polymerization conversion of long chain α-olefins was reached to higher than 95%.

Keywords: Ziegler–Natta catalyst; α-Olefin polymerization; 1-Octene; 1-Decene; Crystallinity

1. Introduction

Researchers have paid a lot of attention to olefin polymerization because of wide applications of these products in industries including films, packaging, lubricants, electrical insulators, inks, petroleum additives, and hot melt adhesives [1–4]. Among the reasons for vast

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*Corresponding author. Email: afshar@aut.ac.ir utilization of these materials, one can mention their wide range of molecular weight from very low to ultra-high [5–7] and stereospecificity from amorphous to very crystalline polymers [8–12]. Ultra-high molecular weight poly α-olefins have several features such as chemical stability, high mechanical strength, nontoxic to human beings, stable viscosity over a wide range, of temperature and excellent compatibility with mineral oil [13, 14].

Polymerization of α-olefins is predominantly carried out by Ziegler–Natta and metallocene catalysts. The polymers produced by single-center metallocene catalysts have low molecular weight with narrow molecular weight distribution [15–19]. However, the productivity of a metallocene catalyst is over a period of 60 min and after this time their activity deteriorates significantly, whereas by Ziegler–Natta catalysts, ultra-high molecular weight polyolefins can be produced [6, 7, 20]. Also, Ziegler–Natta catalysts are able to polymerize α-olefins ranging from irregular and amorphous to highly linear and crystalline structures, due to the chain transfer mechanism. Most titanium based catalysts are not active in olefin polymerization reactions by themselves and require the presence of organometallic cocatalysts [21]. Active species in heterogeneous Ziegler–Natta catalysts are generated in reactions between transition metal species on the surface of solid catalysts and organometallic aluminum compounds. These cocatalysts have common formulation as $AlR_XCl_{(3\text{-}X)}$ [22–24].

All solid Ti-based Ziegler–Natta catalysts contain several types of active centers; therefore, any 1-alkene polymer prepared with a multi-center Ziegler–Natta catalyst can give a mixture of different macromolecules. Some of the centers produce stereospecific polymer molecules, whereas other types of centers produce atactic ones in great excess. The four $TiCl_3$ modifications, α, β, γ, and δ, differ in the crystal arrangement, activity, and stability [21, 25]. As Ziegler catalysts have different types of active centers, molecular weight distribution of polymers prepared using these types of catalysts is broad [26–28]. To improve the yield of the crystalline polymer fraction, compounds such as $MgCl_2$ as supports are added to the catalysts or, alternatively, eliminating this material if the manufacture of atactic polymers is the goal [29–32].

In many cases, other compounds are added to the catalysts. The main roles of electron donor compounds are increasing catalyst stability as well as crystalline polymer fraction [33]. One function of the internal electron donor is to control the amount and distribution of $TiCl_4$ on the surface. Lewis bases (external electron donors) are added in polymerization to produce highly isotactic polypropylene [34]. A high-activity catalyst that can bear modification enough to enhance a specific selectivity would in turn result in a desired product with satisfactory efficiency. Therefore, preparation process and treatment type of these catalysts are important parameters.

This article investigates the production of Ti-based catalysts with high activity and stability that can generate ultra-high molecular weight, amorphous poly(1-octene), poly(1-decene), and their copolymers. These types of polymers are used as drag reducing agents.

2. Experimental

2.1. *Materials*

All procedures were carried out under nitrogen in a Buchi reactor. Hexane was refluxed from metallic sodium under nitrogen for 12 h and distilled before use. Diethylaluminum chloride (DEAC) and triethylaluminum capsules, butyl ether and titanium tetrachloride ($TiCl_4$) were purchased from Aldrich and used without purification. 1-Octene and 1-decene were also purchased from Aldrich and were distilled, collecting the fraction at 60 °C under vacuum before use. The other chemicals were prepared commercially and implemented without purification.

2.2. *Preparation of the catalysts*

C-1: 25 mL $TiCl_4$ was added with a syringe to 300 mL hexane in the 1-L Buchi reactor. The mixture was stirred at 25 °C for a few minutes. After that, 13 mL of DEAC was blended with 200 mL hexane. This solution was gradually added to reactor mixture within 120 min, and then, excess $TiCl_4$ (8 mL) was dropped to the mixture and reaction continued for 60 min. The mixture was washed with hexane at room temperature and eventually dried under vacuum.

C-2: The same procedure was carried out with the only difference being that before introducing additional $TiCl_4$, temperature was raised to 70 °C and reaction continued for 2 h.

C-3: In this procedure, in the first stage, 46 mL butyl ether as internal electron donor with the solvent was added to the reactor. The other stages are similar to the previous reaction (C-2).

C-4: This method is similar to the previous procedure (C-3), except that in C-4 after addition of excess $TiCl_4$, temperature was increased to 105 °C for 15 min and then the mixture was cooled to room temperature.

2.3. *Polymerization*

All polymerizations were carried out in a 1000-mL Buchi reactor equipped with a mechanical stirrer. The reactor was sealed under nitrogen to remove all oxygen and moisture.

Desired amounts of freshly prepared catalyst and $AlEt_3$ with Al/Ti molar ratio of 40 and 400 mL hexane were introduced in this order, and the mixture was stirred for 30 min at 65 °C for precontact. Aging the catalyst at an elevated temperature gave a very active catalyst for polymerization. After that, temperature was decreased to 0 °C, and then, 80 mL monomer was added; the nitrogen pressure was maintained at 2 bar throughout the course of the reaction. The polymerization reaction was stopped after 24 h, terminated by addition of acidified alcohol. After filtering, the residue was washed with alcohol. The obtained precipitate was concentrated under common pressure then heated under vacuum to remove the monomer. The conversion and the catalytic activity of α-olefin polymerization were calculated by the weight of the fraction distilled and of the residue to monomer's weight.

3. Results and discussion

A vacuum Generator ESCALAB MKII spectrometer equipped with twin X-ray anode (aluminum and magnesium) was used for recording of X-ray photoelectron spectra (XPS). These X-ray anodes were operated at 10 kV × 10 mA, and the vacuum in the analysis chamber was maintained better than 5×10^{-8} mbar during analysis. The spectrometer was calibrated using Ag $3d_{5/2}$ photoelectron line [35] at 368.3 eV. Reported values of binding energies are average of at least two different runs and are accurate to ±0.2 eV.

Thermal analysis was performed on a TA Instruments Q100 differential scanning calorimetry (DSC) system using samples in hermetic Al pans. The temperature was raised from 213 to 473 K at a rate of 10 K min^{-1} under nitrogen. T_C and ΔH_m were obtained from the second heating curve. Crystallinity was calculated using PE parameters, that is, ΔH_m 273 J g^{-1} for a 100% crystalline sample.

3.1. *Characterization and performance of catalysts*

Reactions between titanium species and alkyl aluminum cocatalysts invariably result in a significant degree of Ti reduction. Table 1 gives the distribution of Ti valence states in catalyst systems. Obviously, the reduction level depends on the temperature and the presence of electron donor. The energy of the largest Ti peak in XPS spectra, Ti $2p_{3/2}$, is sufficiently sensitive to the valence of Ti atoms. The Ti 2p XPS core-level of ZN catalyst is shown in figure 1.

Ti^{IV} (coordinated to organic ligands): 459.0−459.6 eV
Ti^{III}: 457.0−457.8 eV
Ti^{II}: 456.0−456.1 eV

Since the only valence state of Ti that has catalytic activity is the Ti^{3+}, in the presence of organoaluminum, $TiCl_4$ was alkylated and reduced to become Ti^{3+} which was confirmed as active species for olefins polymerization.

Temperature influence on the performance of Ti-based heterogeneous Ziegler–Natta catalysts is evaluated based on the average stereoregularity of crystalline fractions observed in C-2 catalyst in comparison with C-1; as the temperature increases so does the isospecificity of the active centers.

According to table 1, in the presence of electron donor compound in C-3 and C-4 catalyst systems, activity of the catalyst was higher than C-1 catalyst formulation. By increasing the temperature from 25 to 70 °C, β-form of brown color $TiCl_3$ was converted into δ-$TiCl_3$ with violet color. Meanwhile, by increasing temperature to 105 °C, more crystals of δ-$TiCl_3$ species become stable.

3.2. *Polymer characterization*

The molecular weights of the poly(1-octene) and poly(1-decene) were determined from the intrinsic viscosity of 0–1% solutions of the polymer in THF at 25 °C. The constants of the Mark–Houwink equation were obtained from the literature [36]. Thermal analyses of polymers were carried out by using a DSC. The results of the second scan were reported to eliminate differences in sample history. Table 2 summarizes the results of polymerization.

Table 1. Reduction of Ti species in catalyst–cocatalyst systems.

Catalyst	Ti^{IV} (%)	Ti^{III} (%)	Ti^{II} (%)
C-1	32	24	44
C-2	8	71	21
C-3	7	80	13
C-4	1	96	3

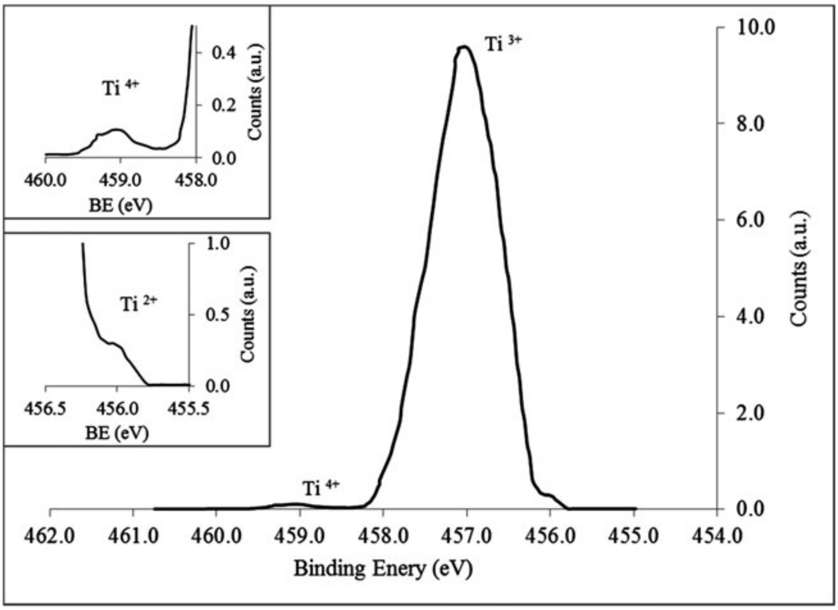

Figure 1. High-resolution XPS of Ti 2p3/2 region of ZN catalyst (C-4).

As mentioned above, with increasing Ti^{3+} content in catalyst systems, the activity of the catalyst and polymerization reaction increased.

Superficially, polymers have different average molecular weights, the lowest in the case of the C-1 catalyst and the highest in the case of C-4 catalyst in the form of δ-$TiCl_3$. According to the results, the C-4 catalyst system displays higher activities toward higher α-olefins with sterically bulkier substituents, 1-decene > 1-octene.

This is remarkable, because an olefin polymerization catalyst generally exhibits lower reactivity toward sterically larger olefins due to steric hindrance. This highly unusual behavior can be explained as follows: A sterically bulkier side chain derived from the last inserted higher α-olefin of the growing polymer chain opens the halide ligands wider, which facilitates the higher α-olefin's coordination to the metal and its insertion into the metal–carbon bond. By increasing the carbon number in the α-olefin chain, selectivity of polymerization

Table 2. Polymerization results of various catalysts and α-olefins.

Polymerization no.	Catalyst	Polymer	Conversion (%)	$M_w \times 10^{-6}$	T_C (°C)	χ_c[a]
1	C-1	Poly(1-octene)	11	0.29	−29.8	<3
2	C-2	Poly(1-octene)	48	0.53	−29.0	<3
3	C-3	Poly(1-octene)	70	0.93	−30.6	5.8
4	C-4	Poly(1-octene)	87	3.57	−29.5	5.0
5	C-4	Poly(1-decene)	96	3.83	−29.6	5.1
6	C-4	Poly(1-octene)/(1-decene)[b]	91	3.82	−30.1	4.1
7	C-4	Poly(1-octene)/(1-decene)[c]	93	4.10	−30.4	3.8

[a] Determined by DSC.
[b] Mass ratio of 1-octene to 1-decene is 1–1.
[c] Mass ratio of 1-octene to 1-decene is 1–3.

reaction is lower. This is a result of the fact that higher α-olefins can form a greater amount of isomers than lower ones in the polymerization cycle. Reactivity of the C-4 catalyst in polymerization of 1-octene and 1-decene is measured by determination of polymerization reaction conversion. As illustrated in figure 2, polymerization of 1-decene is faster than the polymerization of 1-octene, especially in the beginning and the ending stages of the polymerization reaction. This result proves the sterically bulkier substituent's mechanism. One can note that the catalytic activity after 14 h was slightly decreased with increase of polymerization time.

The addition of an α-olefin as comonomer affects not only the polymerization kinetics, but also the polyolefin microstructure. An α-olefin to the polymerization medium is a way to reduce polymer crystallinity. This impact is usually reported as the comonomer effect [37]. When 1-octene and 1-decene are copolymerized with multi-center catalysts, different types of active centers usually produce copolymer molecules of a different composition. Active centers of different types are often formed and decay at different rates. As a consequence, stereoregularity degree of polymers produced with multi-center catalysts decreased with reaction time.

The molecular mass of 1-octene and 1-decene was very similar to each other and therefore, through adding comonomer to polymerization of 1-octene or 1-decene exerted only a few influences on the polymerization kinetics and polymer molecular weight. The existence of 1-octene or 1-decene in polymerization media reduced the efficiency of the catalyst, leading to a negative comonomer effect. This impact was, however, negligible.

In a reaction between the catalyst and a cocatalyst, the active centers are formed in the beginning of polymerization reactions, but these active centers are not stable and the activity of catalysts gradually decreases with reaction time. One of the productive approaches to increase the catalytic activity is stabilization of the active centers. The main method of stabilization is fixing the catalytic systems on the surface of inorganic and organic carriers. Adding butyl ether as internal electron donor in the catalyst system enhanced the catalyst stability and as a result, the activity of the polymerization reaction was greatly improved.

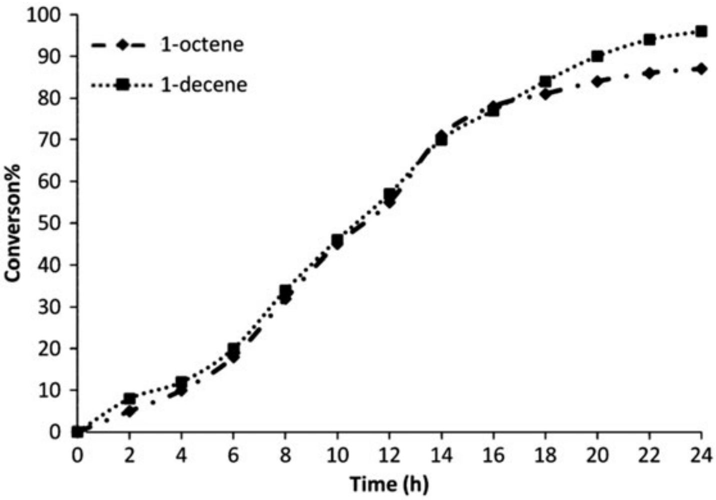

Figure 2. Conversion *vs.* time for the polymerization of 1-octene and 1-decene at 0 °C.

However, they slightly increase content of the crystalline fraction of polymers. Electron donors such as butyl ether selectively poisoned the catalyst sites which made atactic polymer, while the presence of electron donor compounds, decreasing positive charge on a titanium ion, favors the four-center intermediate formation and the olefin insertion into the Ti–C bond. The growing polymer chain attached to an active center exchanged with the ethyl group of cocatalyst molecule, forming M–C_2H_5 bond at the active center and the Al terminated polymer chain. This transfer reaction is common with heterogeneous catalysts.

At the early stages of polymerization reactions, the alkyl groups from the cocatalysts are exchanged with Cl^- in the Ti species and form initial starting chain ends. This reaction caused formation of several cracks on the catalyst. These cracks are the preferred place for the active centers at the earliest stages of polymerization reactions. The first step of the chain growth reaction is the coordination of the C=C bond of α-olefin molecule to Ti through p-bonding. The coordinated monomer is positioned in such a way that its C=C bond is parallel to the M–C bond in the active center. In the second step, the coordinated C=C bond inserts into the M–C bond via the four-center transition state, after which the position of the polymer chain, which is now two carbons longer, and the coordination site are reversed. Chain growth reactions are insertion reactions of C=C bonds of α-olefin molecules into the Ti–C bonds in the active centers.

The interaction of the olefin with the complex took place at the Ti–C bond and the strongly polarized complex, $Cl^{-\delta}AlCl_2(CH_3) \rightarrow Cl_2(CH_3)Ti^{+\delta}$, was the active part. In these reactions, a significant role is also played by the relative charges on the transition metal.

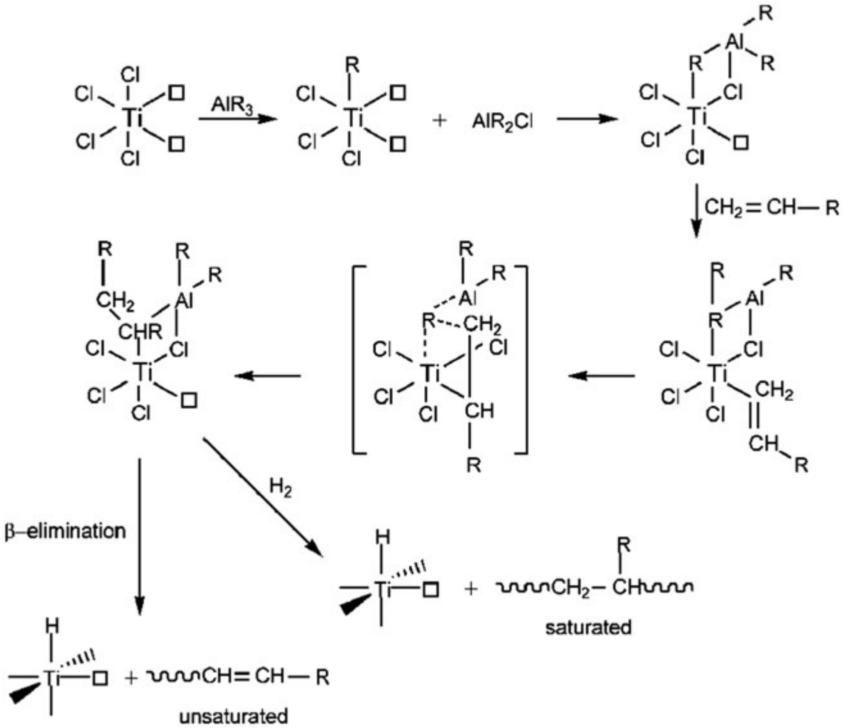

Figure 3. Bimetallic active center proposed for the Ziegler–Natta catalyst and mechanism of α-olefin polymerization [38].

It was possible that chain transfer to hydrogen and/or β-hydrogen elimination predominated as the pathway of chain transfer rather than to alkyl aluminum for 1-octene polymerization. The presence of a positive charge $+\delta$ on the Ti in the $TiCl_4/AlRCl_2$ system leads to considerable acceleration of the reactions of β-elimination of H from the growing chain expressed in decrease of polymerization degree. Mechanism of the α-olefin polymerization by the use of Ziegler catalyst is presented in figure 3.

Donor ligands added to the system $TiCl_4/Et_nAlCl_{3\text{-}n}$ (n = 1,2) increased the catalyst selectivity to linear α-olefins. A reduction in the Ti(IV) ion electron affinity decreased its acidity and increased a coordination mechanism contribution in the whole polymerization reaction, which in turn caused an increase of the product linearity. Using heterogeneous donor-free Ti^{3+} based catalysts having two chloride vacancies gave low isotactic polypropylene while bi- or multinuclear Ti^{3+} species gave isotactic polypropylene.

The active center in Ziegler–Natta catalyst was the metal–carbon bond of the transition metal complex, which was formed by interaction between the main catalyst and cocatalyst of the catalytical system.

4. Conclusion

The preparation method of the catalyst is very important since the properties of the polymer are determined by the catalyst active center. Each different active center produces polymer with different molecular weight and degree of crystallinity. β form of $TiCl_3$ is a low active catalyst while δ-$TiCl_3$ is highly active. Moreover, δ form of $TiCl_3$ is produced by reducing $TiCl_4$ with organoaluminum compounds at increased temperatures. By increasing temperature and/or adding electron donor compounds, δ-$TiCl_3$ becomes more stable.

Catalyst performance and the nature of active titanium species mainly depend on the preparation methodology and the characteristics of each component which are used in catalyst synthesis. Addition of butyl ether as an electron donor resulted in increased catalytic stability. As a consequence, ultra-high molecular weight poly α-olefins can be obtained. The atactic polymer could be synthesized with these heterogeneous catalysts. Prolonged reaction time (24 h) led to an increase in polymer yield to higher than 95%.

References

[1] G. Natta. Italian Patent 554803 (6 December 1955).
[2] G. Natta, I. Pasquon, A. Zambelli, G. Gatti. *J. Polym. Sci.*, **51**, 387 (1961).
[3] P.D. Bolton, P. Mountford. *Adv. Synth. Catal.*, **347**, 355 (2005).
[4] A.T. Lawal, G.G. Wallace. *Talanta*, **119**, 133 (2014).
[5] U. Zucchini, G. Cecchin. *Adv. Polym. Sci.*, **51**, 101 (1983).
[6] Y.V. Kissin. *Macromol. Chem. Macromol. Symp.*, **89**, 113 (1995).
[7] Z.Q. Fan, L.X. Feng, S.L. Yang. *J. Polym. Sci., Part A: Polym. Chem.*, **34**, 3329 (1996).
[8] P. Locatelli, M.C. Sacchi, I. Tritto. *Macromolecules*, **19**, 305 (1986).
[9] M.C. Sacchi, Z.Q. Fan, F. Forlini, I. Tritto, P. Locatelli. *Macromol. Chem. Phys.*, **195**, 2805 (1994).
[10] G. Gui, F. Bao, H. Gao, F. Zhu, Q. Wu. *J. Coord. Chem.*, **59**, 107 (2006).
[11] D. Ribour, V. Bollack-Benoit, V. Monteil, R. Spitz. *J. Polym. Sci., Part A: Polym. Chem.*, **45**, 3941 (2007).
[12] J. Cao, Q.F. Lü. *Polym. Test.*, **30**, 899 (2011).
[13] I.A. Jaber, W.H. Ray. *J. Appl. Polym. Sci.*, **49**, 1709 (1993).
[14] J.P. Claverie, R. Soula. *Prog. Polym. Sci.*, **28**, 619 (2003).
[15] G.H. Robinson, S.G. Bott, J.L. Atwood. *J. Coord. Chem.*, **16**, 219 (1987).
[16] G.G. Hlatky. *Chem. Rev.*, **100**, 1347 (2000).

[17] C. Janiak, K.C.H. Lange, P. Marquardt. *Macromol. Rapid Commun.*, **16**, 643 (1995).
[18] P.G. Belelli, M.L. Ferreira, M.H. Lacunza, D.E. Damiani, A. Brandolin. *Polym. Eng. Sci.*, **41**, 2082 (2001).
[19] P.A. Zapata, H. Palza, L.S. Cruz, I. Lieberwirth, F. Catalina, T. Corrales, F.M. Rabagliati. *Polymer*, **54**, 2690 (2013).
[20] Y.V. Kissin. *J. Polym. Sci., Part A: Polym. Chem.*, **41**, 1745 (2003).
[21] N.E. Morganson, P.G. Bercik. US Patent 4365105 (21 December 1982).
[22] B.I. Kharisov, A.D. Garnovskii, L.M. Blanco, A.S. Burlov, A.G. Luna. *J. Coord. Chem.*, **49**, 113 (1999).
[23] M.J. Yanjarappa, S. Sivaram. *Prog. Polym. Sci.*, **27**, 1347 (2002).
[24] D. Cavallo, L. Gardella, G.C. Alfonso, D. Mileva, R. Androsch. *Polymer*, **53**, 4429 (2012).
[25] L.T. Zhang, Z.S. Fu, Z.Q. Fan. *Macromol. Res.*, **18**, 695 (2010).
[26] J. Skupińska. *Chem. Rev.*, **91**, 613 (1991).
[27] J.C.W. Chein, A. Razavi. *J. Polym. Sci., Part A: Polym. Chem.*, **26**, 2369 (1988).
[28] K.A. Novstrup, N.E. Travia, G.A. Medvedev, C. Stanciu, J.M. Switzer, K.T. Thomson, W.N. Delgass, M.M. Abu-Omar, J.M. Caruthers. *J. Am. Chem. Soc.*, **132**, 558 (2010).
[29] Q. Huang, L. Chen, L. Ma, Z. Fu, W. Yang. *Eur. Polym. J.*, **41**, 2909 (2005).
[30] N. Kashiwa, J. Yoshitake. *Polym. Bull.*, **11**, 479 (1984).
[31] J.C.W. Chien, B.P. Wang. *J. Polym. Sci., Part A: Polym. Chem.*, **26**, 3089 (1988).
[32] D. Ribour, V. Bollack-Benoit, V. Monteil, R. Spitz. *J. Polym. Sci., Part A: Polym. Chem.*, **45**, 3941 (2007).
[33] P. Pino, B. Rotzinger, E.V. Achenbach. *Makromol. Chem. Suppl.*, **13**, 105 (1985).
[34] J.C. Chadwick, G.M.M. Kessel, O. Sudmeijer. *Macromol. Chem. Phys.*, **196**, 1431 (1995).
[35] V.K. Kaushik. *J. Electron Spectrosc. Relat. Phenom.*, **56**, 273 (1991).
[36] J. Brandrup, E.H. Immergut. *Polymer Handbook*, 4th Edn, p. VII/8, Wiley-VCH, Weinheim (1999).
[37] R.A. Hutchinson, W.H. Ray. *J. Appl. Polym. Sci.*, **31**, 1879 (1986).
[38] L.A. Rodriguez, H.M. van Lody, J.A. Gabant. *J. Polym. Sci: Part A-1: Polym. Chem.*, **4**, 1905 (1966).