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Michael Terrier, Marc Visseaux, Thomas Chenal, André Mortreux. Controlled Trans-stereospecific Polymerisation of Isoprene with Neodymium (III) Borohydride-dialkylmagnesium system. *Journal of Polymer Science Part A: Polymer Chemistry*, Wiley, 2007, 45, pp.2400. <10.1002/pola.22002>. <hal-00265642>

**HAL Id: hal-00265642**

**<https://hal.archives-ouvertes.fr/hal-00265642>**

Submitted on 19 Mar 2008

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**Title :** Controlled *Trans*-stereospecific Polymerisation of Isoprene with Lanthanide (III) Borohydride-dialkylmagnesium systems : improvement of activity, selectivity, kinetic studies and mechanistic aspects

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**Abstract :** Neodymium trisborohydride associated to  $MgR_2$  alkylating agents affords an efficient initiator for the stereospecific polymerisation of isoprene. This system presents a good activity (150 kg PI/mol Nd/h; 95% yield in 2 h), is *trans*-stereospecific (up to 97.7%) and the polymerisation shows a quasi-living character. The molecular weights are controlled by the [isoprene]/[Nd] ratio, with a polydispersity index lower than 1.6. A full study is presented here, including the influence of the nature of the alkylating reagent ( $MgR_2$ ), the solvent, the reaction temperature, the  $[MgR_2]/[Nd]$  ratio and replacement of neodymium by other lanthanides. This work also includes a kinetic study of the system and a detailed NMR study of the microstructure of the *trans*-polyisoprene obtained, giving mechanistic insights about the polymerisation reaction.

**Keywords :** neodymium borohydride, isoprene, dialkylmagnesium, *trans*-polyisoprene, polymerisation, catalysis.

## INTRODUCTION

Lanthanides compounds are of great interest in catalysis, especially in polymerisation.<sup>1,2,3</sup> Among the large range of monomers<sup>4,5,6,7,8</sup> that can be polymerised by such catalysts, conjugated dienes have attracted much attention since this area gives rise to a large number of industrial applications with numerous patents.<sup>9,10,11,12</sup> Most of these catalysts consist of complex mixtures that involve binary or ternary systems for the production of *cis*-polydienes. On the other hand, *trans*-polymerisation, far less studied, has attracted a regain of interest since recently, due to the peculiar mechanical properties of *trans*-polydienes<sup>13</sup>. Well-defined organolanthanide-based catalysts have been developed as an alternative to these multicomponent systems,<sup>14,15</sup> in order to improve the control over the molecular weights and molecular weight distribution, what was not possible with the former highly reactive multi-component systems. These molecular catalysts precursors are also of great interest, since they allow a better insight into the polymerisation mechanisms, and also to perform theoretical studies.<sup>16,17,18</sup> However, although these organometallic catalysts exhibit high efficiency, their synthesis may be quite hard to achieve, since they are based on highly sensitive organolanthanide compounds. More simple catalytic systems with good efficiency and control over the polymerisation would be therefore highly desirable. In that context, some work related to the controlled and *trans* stereoselective polymerisation of butadiene has already been reported, where an *in-situ* alkylation method using trisphenoxy neodymium complexes and dialkylmagnesiums have been successfully applied.<sup>19</sup>

On the other hand, the trisborohydrides  $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$  are basic compounds commonly used as precursors in organometallic synthesis.<sup>20,21</sup> They are easily available from the trichlorides in one step by metathetic reaction with  $\text{NaBH}_4$  in THF.<sup>22</sup> Their use for polymerisation of  $\epsilon$ -caprolactone<sup>23</sup>, MMA<sup>24</sup> and styrene<sup>25</sup> has already been investigated and we did communicate preliminary results about the use of a borohydrido neodymium compound associated with a dialkylmagnesium towards isoprene polymerisation.<sup>26,27</sup> This paper presents a full study of this

dual-component initiator, including the influence of temperature, the nature and amount of the solvent, the lanthanide compound and alkylating reagent effects. A kinetic study and some mechanistic aspects of the polymerisation based on a detailed NMR analysis of oligomers are finally reported.

## ***EXPERIMENTAL***

### **Materials**

Solvents were dried over sodium/benzophenone ketyl, deoxygenated by distillation, and stored on molecular sieves (3A) in a glove box. Isoprene (Aldrich) was dried over calcium hydride, distilled twice and stored over molecular sieves (3A) in a glove box. Mg<sup>n</sup>BuEt (BEM, Texas Alkyl, 20% wt heptane), Mg<sup>n</sup>Bu<sub>2</sub> (Aldrich, 1M heptane), Mg<sup>n</sup>Hex<sub>2</sub> (Aldrich, 20% wt heptane) were used as received. Ln(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub> (Ln = Nd, Sm, Y, La) were synthesized as reported in the literature.<sup>22</sup>

### **Polymerisation procedure**

In a glove box, the borohydridolanthanide (4 mg, 1 mmol) was weighed and introduced in a 20 mL flask. Toluene (1 mL), the dialkylmagnesium (1, 2 or 3 equivalents), and the monomer (1000 eq), were added in this order by means of syringes. The flask was taken out of the glove box, and the solution was magnetically stirred at a given temperature for a given time. The flask was then opened to air, and the viscous mixture was diluted with non-dried toluene to quench the polymerisation. The resulting solution was poured into a large volume of a 50/50 methanol/isopropanol mixture containing *tert*-butylcatechol as stabilizing agent. An off-white polymer was filtered off, and dried under vacuum until constant weight.

Two-step polymerisation: the same procedure as described above is used. After polymerisation for 15 minutes, the flask was reintroduced in the glove box. Half of the reaction medium was picked up for analysis. A second crop of isoprene was then added to the above polymer solution, and the

polymerisation was conducted for 2 additional hours before quenching. Analyses were made on this second polymer.

### Polymer characterization

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance 300 at 300 K in  $\text{CDCl}_3$ . Size exclusion chromatography (SEC) was performed in THF as eluent at 20 °C ( $1\text{ mL}\cdot\text{min}^{-1}$ ) using a Waters SIS HPLC-pump, a Waters 410 refractometer and Waters styragel column (HR2, HR3, HR4, HR5E) calibrated with polystyrene standards.

## RESULTS AND DISCUSSION

### Effect of the nature of the alkylating reagent

It has been shown in a preliminary communication<sup>26</sup> that  $\text{AlEt}_3$  moderately activates the precatalyst  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ , affording irregular polyisoprene containing 1,4-*cis* and 1,4-*trans* units. MAO, allylMgBr,  $\text{AlEt}_2\text{Cl}$  and  $\text{Al}^i\text{Bu}_3$  were found unsuitable. On the other hand, dibutylmagnesium was found very active and stereoselective, affording a 95% *trans*-polymer. To extend this work, several dialkylmagnesium compounds were evaluated (Table 1, runs 1 to 5). All of them, associated to  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ , exhibit roughly the same activity with a high conversion within three hours at 50 °C. The control over the molecular weights is satisfactory, the experimental data being close to the calculated ones taking into account only one active R per  $\text{MgR}_2$  (*vide infra*). Polydispersity index values (1.3-1.8) and monomodal GPC curves (see fig. 1) are in accordance with a single-site catalysis (in some experiments a shoulder at higher  $M_n$  values was observed). Finally, as initially observed, all these dialkylmagnesium induce a *trans*-stereospecificity of the polymerisation, up to 96.4% at this temperature. Butylethylmagnesium (BEM) appears to be the best co-catalyst, with regards to these results.

*Table 1.*

*Figure 1.*

### **Effect of the nature of the metal**

According to the literature<sup>28,29</sup> neodymium is by far the most active towards conjugated dienes polymerisation. The same is observed in our case (Table 2). Whereas lanthanum exhibits a poor activity, samarium and yttrium, often studied for comparison, were found totally inactive. Furthermore, neodymium gives rise to the most stereospecific catalytic system among the whole rare earths family.

*Table 2.*

### **Effect of the solvent**

Table 3 shows the results obtained using solvents of different polarity. Toluene (run 6) allows the highest efficiency along with a better control. Using aliphatic solvents (pentane, cyclohexane) reduces the conversion (run 11, 12), but has no influence on the stereospecificity. As expected, the system is inactive in THF (run 14) whereas an excess of 3 THF per neodymium (run 13) inhibits the reaction polymerisation (we observed that 10 additional THF per neodymium totally deactivates the polymerisation). Though chloride solvents have been claimed to be efficient for the *cis*-polymerisation,<sup>5</sup> dichloromethane appears as poorly efficient in our case (run 15). This could be related to: (i) the formation of [Nd]-Cl species that were found less active and stereospecific than [Nd]-BH<sub>4</sub> ones for such polymerisation,<sup>30</sup> (ii) coordination of dichloromethane to the lewis acidic metal site thus preventing isoprene to coordinate. Dilution has little effect on monomer conversion and polymolecularity (runs 16 and 17).

*Table 3.*

## Effect of the polymerisation temperature

While the reaction is nearly finished in less than three hours at 50 °C (Table 4, run 19), the reaction rate decreases (31% yield in three hours) at room temperature (run 18). Nevertheless, such conditions allow to reach the highest *trans*-stereoregularity (97.7%). The influence of the temperature upon stereoselectivity will be discussed later (Table 9). It is noteworthy that the higher the temperature, the broader the polydispersity. This is likely related to termination/transfer reactions occurring more frequently at higher temperatures.<sup>31</sup> Finally, a good compromise between yield and polymer microstructure is found at 50 °C.

### *Table 4.*

## Kinetic studies

The optimal conditions ( $V(\text{toluene}) = 1 \text{ mL}$ ,  $T = 50 \text{ °C}$ ,  $[\text{isoprene}]/[\text{Nd}] = 1000$ ,  $[\text{BEM}]/[\text{Nd}] = 1$ ) were used to determine the kinetics of the polymerisation. Fig. 2 shows the plot of polymer yield versus time. After one hour, the conversion reaches 70%. The maximum of conversion (95%) is obtained within 2 hours under such conditions.

### *Figure 2.*

The initial activity measured at low conversion is higher than 150 kg of polymer/mole Nd/h at 50 °C (Table 5, run 24), which is 150 times the one mentioned for the comparable  $\text{NdCl}_3(\text{THF})_3/\text{MgR}_2$  system.<sup>2</sup> This can be explained by the higher solubility of the borohydride compounds compared to that of the chloride analogues. Such an activity is the highest obtained for a *trans*-stereospecific lanthanide-based catalytic system.<sup>32</sup>

A linear first-order kinetic plot was obtained under the standard conditions, which corresponds to a constant number of active species throughout the polymerisation. The apparent rate constant, obtained from the plot  $\text{Ln}(1/(1 - \text{Yield}))$  vs. time (fig. 3), could be estimated at  $22.3 \times 10^{-3} \text{ min}^{-1}$  ( $1.34 \text{ h}^{-1}$ ) at  $50 \text{ }^\circ\text{C}$ , which is in the common range generally observed.<sup>33,34</sup>

### *Figure 3*

Several experiments were carried out at different temperatures and stopped at low conversion in order to determine the apparent activation energy of the reaction. Results are shown in table 5 (runs 22 to 25) and figures 4 and 5. The polymerisation was remarkably accelerated by raising the temperature. The activation energy,  $75 \text{ kJ/mol}$  ( $\Delta H^\circ = 75 \text{ kJ/mol}$ ;  $\Delta S^\circ = -241 \text{ J/K/mol}$ ), is again in agreement with literature values.<sup>35,36</sup>

### *Table 5.*

### *Figure 4.*

### *Figure 5.*

## **Influence of the [BEM]/[Nd] ratio**

### *Table 6.*

The influence of the [BEM]/[Nd] ratio on the molecular weight was investigated. Table 6 compares experiments using one to five equivalents of BEM.

When a stoichiometric amount of BEM is associated to  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  (run 27), molecular weights are in accordance with one growing chain per Mg and thus per neodymium, taking in account the yield of polymer. For two equivalents of BEM per neodymium (run 28), the experimental molecular weights ( $M_{n \text{ exp}}$ ) are close to the calculated ones ( $M_{n \text{ calc}}$ ) on the basis of two



growing chains per neodymium (Taube has mentioned the possibility of two and three polybutadiene growing chains on a neodymium from a  $\text{Nd}(\text{C}_3\text{H}_5)_3$  initiator<sup>7</sup>). Considering that the *trans*-stereospecific character is preserved, all these results tend to show that, in our standard conditions, the same mechanism may be involved<sup>27</sup> in the presence of two equivalents of BEM with one alkyl group active per dialkylmagnesium only, rather than Nd/Mg transfer reactions, which would possibly modify the stereoselectivity.

Adding three equivalents of  $\text{MgR}_2$  or more dramatically slows down the polymerisation (runs 29 to 32). The reaction medium takes an intense green color, which could be related to the formation of allyl species.<sup>37</sup> In this case, a small quantity of polyisoprene, rich in 3,4-defects, could be isolated, but only after a prolonged time or a higher polymerisation temperature (Table 6, runs 31 and 32). This probably excludes the possibility of transfer reactions between neodymium and magnesium in the standard conditions. Steric hindrance around the neodymium atom could be proposed<sup>7</sup>: three growing chains per neodymium, together with the presence of borohydrido moieties, might saturate the environment of the metal, thus preventing the access of the monomer to neodymium. In that context, we observed that the addition of one equivalent of a ligand supposed to favour the dissociation of aggregated neodymium species (*i.e.* ethylenediamine, hexamethylenediamine, THF), to a mixture containing three equivalents of BEM per Nd, had no benefit in terms of reactivity.

With a half equivalent of dialkylmagnesium (run 26), a deviation with respect to the control over molecular weights is observed (61500 vs. 96600). This indicates that more than one R per Mg is active in such conditions. However, if both alkyl groups of each dialkyl magnesium had been involved in the process, the molecular weights would have been even lower ( $M_n = 48300$  for two active R per Mg).

## Controlled character of the polymerisation

The plot of the molecular weights versus yield is a straight line, which indicates that each polymer chain regularly grows with monomer conversion (see fig. 6) as expected for a controlled polymerisation. Furthermore, the polydispersity index remains in the range 1.3-1.6, which is indicative of the presence of single-site active species in the reaction medium all along the process. This is also confirmed by the monomodal GPC curves obtained (see fig. 1).

### *Figure 6.*

Moreover, from the two-step polymerisation experiment at 50 °C shown in figure 7, the GPC profiles of polyisoprene obtained at the first step (68% yield, 15 min) moved to a higher molecular weight value (second step, 158% yield, total time 2 h 15 min), keeping a relatively narrow molecular weight distribution, indicative of an apparently living process.

### *Figure 7.*

The control over the polymerisation being relatively well established, it was possible to modulate the length of the polymer chain from the [monomer]/[neodymium] ratio. Some results are presented in table 7 (runs 27 and 33 to 36). Although the polydispersity index becomes larger, the calculated molecular weights are in quite good agreement with the experimental ones. It is noteworthy that the *trans*-stereospecificity, albeit lower in the case of higher [isoprene]/[Nd] ratios, is roughly maintained.

### *Table 7.*

## Microstructure of the polymers

The process described in this paper is a rare example of *trans*-stereospecific polymerisation of isoprene. We have studied the effect of several parameters on the stereoselectivity, in order to determine the best operating conditions. As shown in table 8, a temperature variation notably influences the stereoselectivity.

**Table 8.**

The standard conditions were fixed as 50 °C which is a good compromise *trans* rate / monomer conversion (i.e. 95.5 – 92% in 3 h). At room temperature, the *trans*-stereoregularity of the polymer reaches 97.7% but the conversion is lower (31% in 3 h). At higher temperatures (runs 16, 17), the activity is notably increased but the *trans*-stereoregularity decreases.

## Mechanistic study from NMR end-groups analysis

With the aim to get a better understanding of the mechanism, a <sup>13</sup>C NMR analysis of a low molecular weight polyisoprene was performed in order to assign all signals, including chain-end groups. This study was made with a polyisoprene initiated with the Nd(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub> / di-n-hexylmagnesium system. This co-catalyst was used in a sake of simplicity as it only gives one type of initiating group.

**Figure 8.**

As shown in figure 8, the stereoselectivity is essentially *trans* with *cis* and 3,4 defects. This can be calculated from the relative integrations of the methyl signals : CH<sub>3</sub> *trans* at 16.0 ppm (92%), CH<sub>3</sub> *cis* at 23.4 ppm (7%) and CH<sub>3</sub> 3,4 at 18.6 ppm (1%)<sup>38</sup>. The n-hexyl end-group coming from the initiation step (see fig. 4) is found at 14.1(CH<sub>3</sub>), 22.7(α-CH<sub>2</sub>), 32.2 (β-CH<sub>2</sub>), 29.8 ppm (δ-CH<sub>2</sub>). The two next CH<sub>2</sub> are attributed to 29.3 (γ-CH<sub>2</sub>) and 27.9 ppm (ε-CH<sub>2</sub>) due to their proximity

to the double-bond. The relative intensity of the end-group CH<sub>3</sub> signal is 1/41 with respect to that of the CH<sub>3</sub> signal of the isoprene unit : this corresponds to a DP<sub>n</sub> = 41 and M<sub>n</sub> = 2300 g/mol.

Lanthanides-based diene polymerisation catalysts generally involve allyllanthanide active species. Considering that the polymerisation under study is quasi living, the major process of termination likely proceeds through the final hydrolysis step with methanol (followed by precipitation, see experimental part). The <sup>13</sup>C resonances attributed to a first type of chain-end (scheme 1) are located at 17.7 and 25.7 ppm, corresponding to vicinal Z and E methyl groups (DEPT experiments), respectively at 131.2 and 124.8 ppm for the quaternary and ternary carbons of the last double-bond. This type of chain end is the major one (ca. 80%) and is characteristic of a 1,4-*trans*-addition, with hydrolysis at the terminal carbon.

#### *Scheme 1.*

The presence of a second type of ending (20% relative integration), corresponding to a terminal =CH-CH<sub>3</sub> pattern, is shown by the signals at 13.3 and 118.3 ppm. This type of end-group is characteristic of a 4,1-*trans* addition of the last monomer, with again hydrolysis at the last carbon (second type, scheme 2).

#### *Scheme 2.*

To complete this study, careful examination was made on the residual signals of the spectrum. The resonances depicted at 147.7(a), 111.2(b), 47.2(c), 37.5(d), 32.2(e), 31.2(f) and 18.6(g) are attributed to 3,4-defects between two 1,4-*trans* sequences. They have a quite identical intensity which corresponds to a *ca* 1% error rate. Such defects could also arise from σ-π allylic rearrangement following a classical 1,4-insertion mode (scheme 3). The hypothesis of formation of

pure, homo 3,4-PI in a 1% relative quantity should be rejected because (i): one typical NMR signal doesn't correspond to pure 3,4-PI (the one at 47.2 ppm), and (ii): the GPC of the whole polymer displays a monomodal character which demonstrates the presence of one type of polymer only, i.e. the 1,4-*trans*-polyisoprene containing 1% of 3,4-defects. The only possible mechanism is then the 1,4-addition (or 3,4- which gives the same) on the internal carbon of the allylic species with protonolysis of the last carbon. The same interpretation can be given for the results published by Masuda et al. in the case of 7% 3,4-errors in a 1,4-*cis*-polyisoprene<sup>39</sup>.

### *Scheme 3*

## **Conclusion**

A detailed study on the polymerisation of isoprene using lanthanide trisborohydride / dialkylmagnesium combinations has been performed. The system has been largely optimised with respect to the preliminary results published, and gives a better understanding of the mechanism of the reaction. The ideal parameters allowing the synthesis of polyisoprenes of controlled macromolecular data along with high *trans*-regularity have been determined. As expected, the temperature has been shown to have some influence on the nature of the polymer obtained. It is now unambiguously established that the polymerisation displays an apparently living character, which is of interest for our on going studies on the synthesis of block copolymers using these simple and useful *in situ* catalytic systems. Further work is in progress in that direction.

1. Arndt, S.; Okuda, J. *Chem Rev* 2002, 102, 1953.
2. Hou, Z.; Wakatsuki, Y. *Coord Chem Rev* 2002, 231, 1.
3. Gromada, J.; Carpentier, J-F.; Mortreux, A. *Coord Chem Rev* 2004, 248, 397.
4. Yasuda, H.; *J Polym Sci Part A: Polym Chem* 2001, 39, 1955.
5. Visseaux, M.; Chenal, T.; Roussel, P.; Mortreux, A.; *Journal of Organometallic Chemistry* 2006, 691, 86.
6. Dong, M.; Masuda, T.; *Polymer* 2003, 44, 1561.
7. Sánchez-Barba, L. F.; Hughes, D. L.; Humphrey, S. M.; Bochmann, M.; *Organometallics* 2005, 24, 3792.
8. Maiwald, S.; Sommer, C.; Müller, G.; Taube, R.; *Macromol Chem Phys* 2002, 203, 1029.
9. Boisson, C.; Monteil, V.; Spitz, R.; Barbotin, F.; *Macromol Chem Phys* 2003, 204, 1747.
10. Stoye, H.; Thiele, S. K-H.; Monroy, V.; Wilson, D. R. (Dow Global Technologies Inc.). World Patent 033,545 (2003).
11. Laubry, P. (Michelin). World Patent 38,636 (2002).
12. Halasa, A. F.; Hsu, W-L.; Jasiunas, C. A.; Sandstrom, P. H.; Beers, R. N. (Goodyear). European Patent 1,593,528 (2005).
13. Song, J.-S.; Huang B.-C.; Yu D.-S. *J. Appl. Pol. Sci.* 2001, 82, 81.
14. Kaita, S.; Hou, Z.; Nishiura, M.; Doi, Y.; Kurazumi, J.; Horiuchi, A. C.; Wakatsuki, Y. *Macromol Rapid Commun* 2003, 24, 179.
15. Cui, L.; Ba, X.; Teng, H.; Ying, L.; Li, K.; Jin, Y. *Polymer Bulletin* 1998, 40, 729.
16. Kwag, G.; Lee, J-G.; Bae, C.; Lee, S. N. *Polymer* 2003, 44, 6555.
17. Schinzel, S.; Bindl, M.; Visseaux, M.; Chermette, H. *J. Phys. Chem. A.* 2006, 110, 11324.
18. Lio, Y.; Baldamus, J.; Tardiff, O.; Hou, Z. *Organometallics* 2005, 24, 4362.
19. Gromada, J.; Le Pichon, L.; Mortreux, A.; Leising, F.; Carpentier, J-F. *Journal of Organometallic Chemistry* 2003, 683, 44-55.
20. Cendrowski-Guillaume, S. M.; Le Gland, G.; Nierlich, M.; Ephritikhine, M. *Organometallics* 2000, 19, 5660.
21. Barbier-Baudry, D.; Blacque, O.; Hafid, A.; Nyassi, A.; Sitzmann, H.; Visseaux, M. *Eur J Inorg Chem* 2000, 2333.
22. Mirsaidov, U.; Shaimuradov, I. B.; Khikmatov, M. *Russ J Inorg Chem* 1986, 31, 753.
23. Guillaume, S. M.; Schappacher, M.; Soum, A. *Macromolecules* 2003, 36, 54.
24. Barbier-Baudry, D.; Bouyer, F.; Sofia, A.; Madureira B.; Visseaux, M. *Appl. Organometal. Chem.* 2006, 20, 24.
25. Zinck, P.; Visseaux, M.; Mortreux, A. *Z. Anorg. Allg. Chem.* 2006, 632, 1943-1944.
26. Bonnet, F.; Visseaux, M.; Pereira, A.; Bouyer, F.; Barbier-Baudry, D. *Macromol Rapid Commun* 2004, 25, 873.
27. Bonnet, F.; Visseaux, M.; Pereira, A.; Barbier-Baudry, D. *Macromolecules* 2005, 38, 3162.
28. Wilson, D. J. *Polymer International* 1996, 39, 235.
29. Evans, W. J.; Giarikos, D. G. *Macromolecules* 2004, 37, 5130.
30. Urazbaev, V. N.; Efimov, V. P.; Sabirov, Z. M.; Monakov, Y. B. *J Appl Pol Sci*, 2003, 89, 601.
31. Odian, G. in "Principles of Polymerisation", 3<sup>rd</sup> edition, J. Wiley & Sons, Inc, Polytechnica, New York, 1994.
32. Ajellal, N.; Furlan, L.; Thomas, C. M.; Casagrande, O. L.; Carpentier, J.-F. *Macromol Rapid Commun* 2006, 27, 338.
33. Cai, X.; Gong, Z.; Wang, F. *Macromol Chem Phys* 1996, 197, 1449.
34. Maiwald, S.; Weissenborn, H.; Sommer, C.; Müller, G.; Taube, R. *J Organomet Chem* 2001, 640, 1.
35. Costabile, C.; Guerra, G.; Longo, P.; Pragliola, S.; *Macromolecules* 2005, 38, 6327.
36. Xiaoping, C.; Zhi, G.; Fosong, W.; Xinghao, Z.; Xiuhua, L. *Academia Sinica* 1995, 6, 653.
37. Taube, R.; Maiwald, S.; Sieler, J. *J Organomet Chem* 2001, 621, 327.
38. Li, F.; Jin, Y.; Pei, F.; Wang, F. *J.M.S.-Pure Appl Chem* 1994, A31(2), 273.
39. Dong, W.; Masuda, T. *J Polym Sci, Part A: Polym Chem* 2002, 40, 1838.