

# In Situ Copolymerization of Ethylene to Produce Linear Low-Density Polyethylene by $\text{Ti}(\text{OBU})_4/\text{AlEt}_3\text{-MAO}/\text{SiO}_2/\text{Et}(\text{Ind})_2\text{ZrCl}_2$

Bochao Zhu,<sup>1</sup> Cunyue Guo,<sup>2</sup> Zhongyang Liu,<sup>2</sup> Yuanqi Yin<sup>1</sup>

<sup>1</sup>Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China

<sup>2</sup>CAS Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science & Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Received 15 January 2004; accepted 2 June 2004

DOI 10.1002/app.21190

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Linear low-density polyethylene (LLDPE) is produced in a reactor from single ethylene feed by combining  $\text{Ti}(\text{OBU})_4/\text{AlEt}_3$ , capable of forming  $\alpha$ -olefins (predominantly 1-butene), with  $\text{SiO}_2$ -supported  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$  (denoted  $\text{MAO}/\text{SiO}_2/\text{Et}(\text{Ind})_2\text{ZrCl}_2$ ), which is able to copolymerize ethylene and 1-butene in situ with little interference in the dual-functional catalytic system. The two catalysts in the dual-functional catalytic system match well because of the employment of triethylaluminum ( $\text{AlEt}_3$ ) as the single cocatalyst to both  $\text{Ti}(\text{OBU})_4$  and  $\text{MAO}/\text{SiO}_2/\text{Et}(\text{Ind})_2\text{ZrCl}_2$ , exhibiting high polymerization activity and improved properties of the obtained polyethylene. There is a noticeable

increment in catalytic activity when the amount of  $\text{Ti}(\text{OBU})_4$  in the reactor increases and 1-butene can be incorporated by about 6.51 mol % in the backbone of polyethylene chains at the highest  $\text{Ti}(\text{OBU})_4$  concentration in the feed. The molecular weights ( $M_w$ ), melting points, and crystallinity of the LLDPE descend as the amount of  $\text{Ti}(\text{OBU})_4$  decreases, which is attributed mainly to chain termination and high branching degree, while the molecular weight distribution remains within a narrow range as in the case of metallocene catalysts. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2451–2455, 2004

**Key words:** copolymerization; polyethylene; linear

## INTRODUCTION

For the past 2 decades, metallocene catalysts<sup>1</sup> have made a profound impact on polyolefin technology<sup>2</sup> for their excellent properties of high catalytic activity and stereoregularity. These types of compounds can incorporate a variety of comonomers with ethylene<sup>3–5</sup> to produce linear low-density polyethylene (LLDPE) with narrow molecular weight distribution (MWD)<sup>6,7</sup> and comonomer distributions without obvious loss of processability.<sup>8a</sup>

An alternative route employing a homogeneous two- or three-component catalytic system to synthesize LLDPE with single feed ethylene through tandem copolymerization (in situ copolymerization as mentioned herein) was first systematically investigated by Bazan and co-workers.<sup>8b–8e</sup> Their work ignited enormous interests both in academic and in technological fields for the convenience and low cost in fabricating

tailored branched polyethylene under mild conditions. In addition, among previous studies, some dual-functional catalyst system, such as  $\text{Ti}(\text{OC}_3\text{H}_7)_4\text{-TiCl}_4/\text{MgCl}_2/\text{PE-Al}(\text{C}_2\text{H}_5)_3$ , have been attempted to produce LLDPE.<sup>9</sup> These catalytic systems contain two catalysts, of which one is a dimerization catalyst,  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ , and the other is a typical Ziegler–Natta catalyst,  $\text{TiCl}_4/\text{MgCl}_2/\text{PE}$ . However, only polyethylene of low branching degree is prepared due to inferior copolymerization of Ziegler–Natta catalysts.

Contrary to conventional Ziegler–Natta catalysis where the comonomer is mainly incorporated into the low molar mass fraction, comonomer insertion into the polymer chain is solely statistical for polymers obtained with metallocene catalysts. Thus the substitution of metallocene catalyst for Ziegler–Natta catalyst as a strategy to enhance the polymer properties is currently interesting in a dual-functional catalytic system because 1-alkenes produced with oligomerization catalyst can be effectively incorporated to form branched polyethylene in situ. Since metallocene catalysts can only be activated by unique cocatalyst methylaluminoxane (MAO), other activators like triethylaluminum ( $\text{AlEt}_3$ ) to ethylene oligomerization catalyst would affect metallocene's catalytic activity and monomer insertion rates etc. A major limitation to this approach comes from chemical interferences between

Correspondence to: C. Guo (cyguo@iccas.ac.cn).

Contract grant sponsor: "863" Project; contract grant number: 2002AA333050; contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50103012.

TABLE I  
Polymerization Results of the Dual-Functional Catalytic System<sup>a</sup>

Run	Ti/Zr mol/mol	AlEt <sub>3</sub> /Ti mol/mol	Incorp mol%	Activity <sup>b</sup>	T <sub>m</sub> °C	M <sub>w</sub> × 10 <sup>-4</sup> g/mol	MWD	d <sub>25</sub> g/cm <sup>3</sup>
1	0	0	0	1.88	133.2	31.4	3.921	0.960
2	0.25	8	3.78	5.57	116.9	22.6	3.620	0.929
3	0.75	8	5.16	5.14	109.2	22.4	2.733	0.918
4	1.125	8	6.51	3.64	96.8	23.2	2.415	0.901
5	0.75	16	4.91	3.17	98.6	19.5	2.151	0.911
6	0.75	24	4.16	4.61	114.5	21.2	1.865	0.920
7	0.75	32	3.68	3.31	115.9	33.4	1.543	0.924

<sup>a</sup> Conditions: 100 mL of toluene; ethylene pressure = 0.1 MPa; temperature = 50°C; preoligomerization time = 5 min; copolymerization time = 30 min, Zr = 4 μmol

<sup>b</sup> 10<sup>6</sup> g (mol Zr · h)<sup>-1</sup>

the two catalysts and different responses to reaction conditions.<sup>10</sup>

This paper provides a way of reducing to the utmost extent the interference in a dual-functional catalytic system by anchoring a metallocene compound onto MAO-activated silica where the bound MAO acts as cocatalyst to the metallocene catalyst,<sup>11</sup> thus greatly lessening the adverse effect of AlEt<sub>3</sub> on the metallocene compound. This process, in particular, can produce polyethylene of spherical morphology while AlEt<sub>3</sub> plays a double role of activator to ethylene oligomerization catalyst Ti(OBu)<sub>4</sub> and scavenging agent in the reaction system.

## EXPERIMENTAL

### Materials

All operations were carried out in a nitrogen atmosphere. Commercial toluene was purified by refluxing over metallic sodium using benzophenone as an indicator. Polymerization grade ethylene was dried and deoxygenated by molecular sieves and a reduced Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Commercial Ti(OBu)<sub>4</sub> was purified by molecular sieves. MAO; AlEt<sub>3</sub> and Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> catalyst were purchased from Aldrich Co. and used as received. Grace 955 No. SiO<sub>2</sub> was purchased from Davison Co.

### Immobilization of Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> on SiO<sub>2</sub>

Silica (3 g) was heated for 12 h at 400°C under N<sub>2</sub> and then at 150°C in vacuo for 6 h. The product was suspended in a solution of MAO (1.4 mol/L in toluene) and reacted at 60°C for 3 h. It was filtered in a Schlenk apparatus and washed several times with toluene until no more Al was found in the washing. This MAO/SiO<sub>2</sub> was added to 60 mL of toluene containing 0.2859 g of Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>, stirred overnight, washed with toluene, and filtered until no more Zr was found in the washing prior to drying in vacuo. This SiO<sub>2</sub>-supported catalyst contains 0.56 wt % Zr.

### Ethylene polymerization

To a 250-mL thermostated flask were added 100 mL of toluene and the desired amount of AlEt<sub>3</sub>. The mixture was stirred for a while before a predetermined amount of Ti(OBu)<sub>4</sub> was transferred at the desired reaction temperature and ethylene pressure. The required amount of MAO/SiO<sub>2</sub>/Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> was added 5 min later and the copolymerization was terminated after 30 min by the addition of ethanolic hydrochloric acid (10 vol % ethanolic solution). The polyethylene was kept in excess of 10 vol % ethanolic solution overnight and washed with ethanol and water in a Büchner funnel, separated, and dried until constant weight at 70°C in vacuo.

### Characterization

The M<sub>w</sub> and MWD of polyethylene were determined by GPC at 140°C using *o*-dichlorobenzene-d<sup>4</sup> as solvent. <sup>13</sup>C-NMR analyses were performed at 80°C on a Varian XL-300 spectrometer using *o*-dichlorobenzene-d<sup>4</sup> as solvent. Calorimetric measurements were carried out on a Perkin-Elmer DSC-7 calorimeter at a heating rate of 10°C/min. The heat of fusion of a

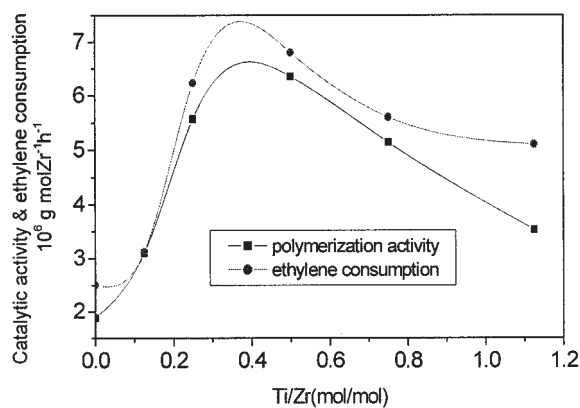


Figure 1 Effect of Ti /Zr ratio on activity.

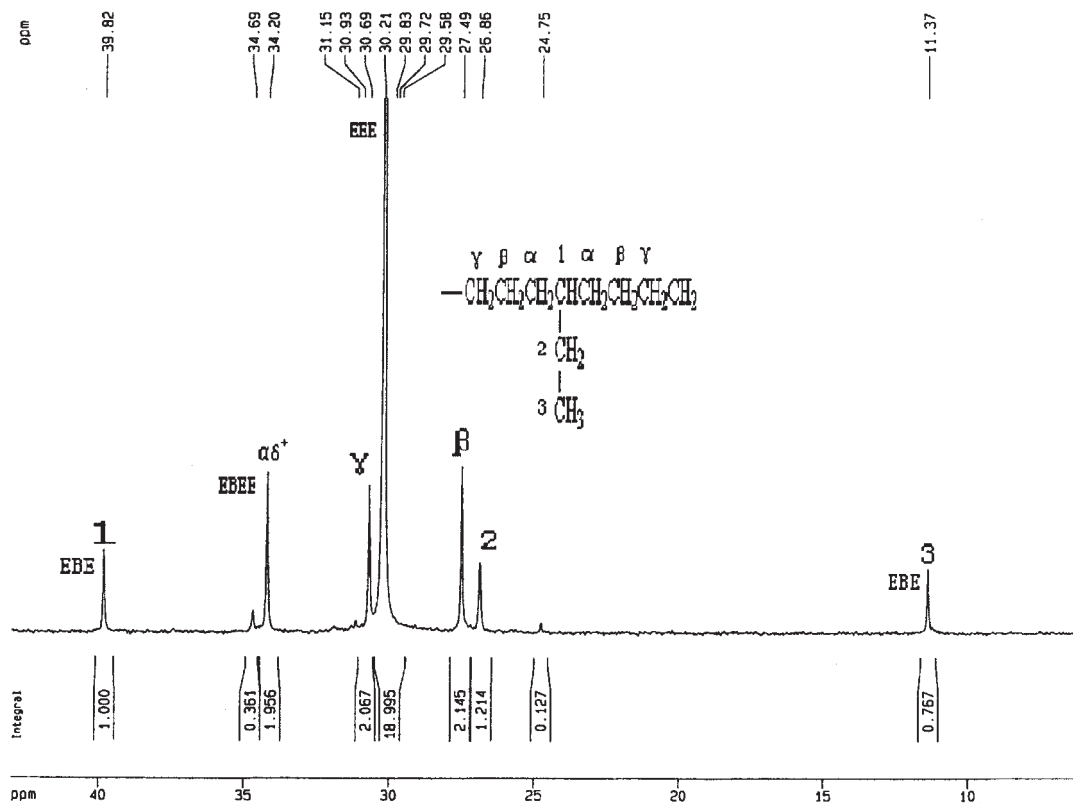


Figure 2  $^{13}\text{C}$ -NMR spectrum of branched polyethylene.

perfect crystal used for the determination of the crystallinity was taken as 290 J/g.

## RESULTS AND DISCUSSION

MAO containing different amounts of alkylaluminum has been known to have great influences on the reactivity, molecular weight, and even structure of polyethylene.<sup>12</sup> This characteristic provides the possibility of combining MAO with a suitable amount of  $\text{AlEt}_3$  to form cocatalysts in the dual-functional catalytic system.  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$  is herein contacted with MAO fixed on  $\text{SiO}_2$  during the immobilization process to form a copolymerization catalyst, thus preventing  $\text{AlEt}_3$  from reacting with metallocene. Thus, there is little interference between the two catalysts in the dual-functional catalytic system because  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ , on reaction with MAO fixed on the surface of  $\text{SiO}_2$  in advance during the immobilization process, forms the active species complex.<sup>13</sup>

Listed in Table I are results of ethylene copolymerization using this catalytic system. The lowest density of the resultant polyethylene reached  $0.901 \text{ g/cm}^3$ , much lower than that of its homopolymerization counterpart of  $0.960 \text{ g/cm}^3$ . The data also show that the catalytic activities and properties of polyethylene varied under different reaction conditions as detailed thereafter.

Figure 1 shows the effect of Ti/Zr ratio on ethylene consumption rate and polymerization behavior in the dual-functional catalytic system. Figure 1 shows that the two catalysts are well matched. When the Ti/Zr ratio varies from 0 to 1.0, 1-butene produced in the oligomerization is almost completely incorporated into LLDPE. The catalytic activity of this dual-functional catalytic system is enhanced as the  $\text{Ti}(\text{O}i\text{Bu})_4$  concentration increases in the reaction medium until reaching maximum values. It can be increased by about threefold for ethylene polymerization compared with the re-

TABLE II  
Sequence Distribution of Polyethylene Obtained

Run	BBB	BBE	BEB	EBE	BEE	EEE	B%	E%	$\eta_B$	$\eta_E$
2	0	0	0.015	0.082	0.119	0.784	3.83	96.4	0.44	11.7
4	0	0	0.014	0.115	0.208	0.541	6.51	93.5	0.56	8.12

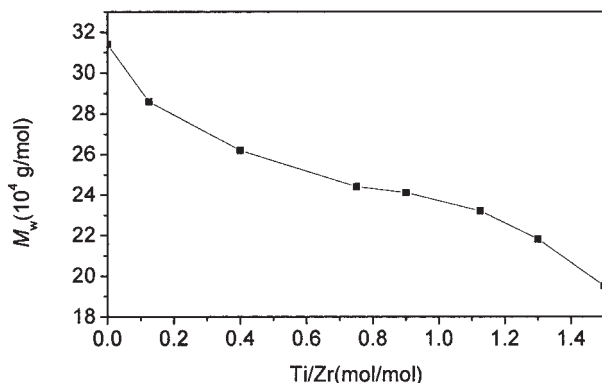


Figure 3 Relationship between  $M_w$  and Ti/Zr ratio.

sults from using MAO/SiO<sub>2</sub>/Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>, in agreement with results reported for the copolymerization of small-size  $\alpha$ -olefins<sup>5,14</sup> (usually 1-butene, 1-hexene, or 1-octene) with ethylene by metallocene catalysts.

The <sup>13</sup>C-NMR spectrum of polyethylene prepared with the dual-functional catalysis system is shown in Fig. 2. The spectrum indicates that polyethylenes obtained from runs 2 to 7 are short branched.

Calculated results of the sequence distribution of obtained polymers are summarized in Table II by method of Linderman and Adams.<sup>15</sup> Data in Table II show that the incorporation rate of 1-butene in the polymers increases with increasing Ti(OBu)<sub>4</sub> amount in the dual-functional reaction medium, reaching a value of 6.51 mol % incorporation for the highest Ti(OBu)<sub>4</sub> concentration used. All of the 1-butene units in the copolymers were isolated between ethylene units and no blocks of 1-butene were found. Similar results were obtained for other  $\alpha$ -olefins copolymerized over metallocene catalysts.<sup>16</sup>

The effect of Ti/Zr ratio on polymer molecular weight is shown in Fig. 3. With the increase of the Ti/Zr ratio in the dual-functional catalytic system,  $M_w$  descends from greater than 300,000 to about 180,000. This is attributed to the fact that more oligomerization

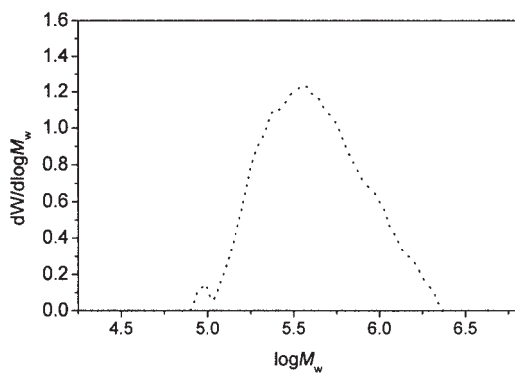


Figure 4 GPC curve of polyethylene.

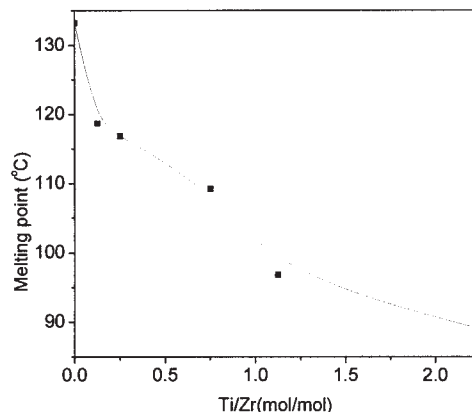


Figure 5 Relationship between melting point and Ti/Zr ratio.

catalyst leads to the production of more 1-butene, hence stabilizing the single active center and offering more opportunities for  $\beta$ -H elimination or monomer transfer reaction to occur.<sup>17</sup>

Figure 4 shows the GPC curve of polyethylene of run 7. Table I shows that polymers (runs 2 to 4) have relatively narrow MWD values and tend to become narrower (from 3.921 to 2.415) with increasing amount of Ti(OBu)<sub>4</sub>, in agreement with that of conventional copolymerization with metallocene catalysts.<sup>6</sup>

Figure 5 shows that the melting points of polymers decrease with increasing Ti/Zr ratio. It is easy to get the polymers with lower melting points from run 1 of 133.2°C to run 4 of 96.8°C by this dual functional catalytic system. It provides a way to adjust properties of the polymer by designing reaction conditions. The melting points and density of polyethylene decrease with increasing amount of Ti(OBu)<sub>4</sub> but exhibit no obvious correlation with the increment of AlEt<sub>3</sub>, mainly due to the fact that more frequent branching gives rise to more disordered polymer morphology.

The crystallinity, as expected, decreases remarkably with increasing Ti/Zr ratio in the dual-functional catalytic system as shown in Fig. 6, declining from 70 to 18% with increasing Ti/Zr value from 0 to 1.125.

## CONCLUSION

LLDPE with the properties described above was prepared in situ using ethylene alone as the feed. Adverse effects of alkylaluminum on metallocene catalyst are reduced to the greatest extent through the immobilization of Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> on MAO-treated SiO<sub>2</sub> where the fixed MAO acts as cocatalyst of Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>. The  $\alpha$ -olefins formed during ethylene oligomerization catalyzed by Ti(OBu)<sub>4</sub>/AlEt<sub>3</sub> can be copolymerized effectively with ethylene to form LLDPE of better morphology under MAO/SiO<sub>2</sub>/Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> without adding comonomers from the outside. The properties of LL-

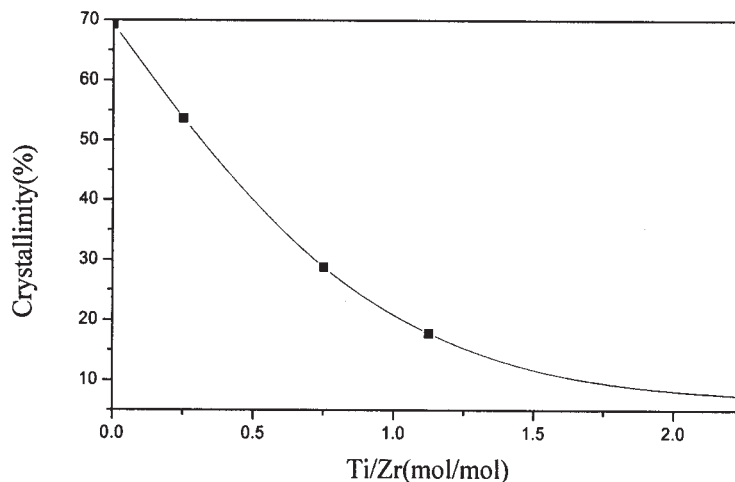


Figure 6 Relationship between crystallinity and Ti/Zr value.

DPE can be adjusted conveniently through regulation of the reaction conditions, in particular the ratio of the two metals. Methods for the solution of the problem of interference accompanying the two metal sites during ethylene copolymerization foretell potential commercial uses of this kind of dual-functional catalytic system, although there is still a long way to go due to engineering problems.

## References

1. Thayer, A. M. *Chem Eng News* 1995, 11, 15.
2. Montagna, A. A. *Chemtech* 1995, 34, 44.
3. Heiland, K.; Kaminsky, W. *Makromol Chem* 1992, 193, 601.
4. Mathot, V. F.; Sherenberg, R. L.; Pijpers, M. F. J.; Bras, W. J. *Therm Anal* 1996, 46, 681.
5. Quijada, R.; Rojas, R.; Mauler, R. S.; *J Appl Polym Sci* 1997, 64, 2567.
6. Chien, J. C. W.; He, D. W. *J Polym Sci Polym Chem* 1991, 29, 1585.
7. Quijada, R.; Jairton, D.; Mauler, R. S. M.; Rosangela, B. S.; Griselda, B. G. *Macromol Chem Phys* 1995, 196, 3991.
8. (a) Beek, J. A. M. van; Doremaele, G. H. J. van; Gruter, G. J. M.; Arts, H. J.; Eggels, G. H. M. WO 96/13529 1996; (b) Komon, Z. J. A.; Bu, X. H.; Bazan, G. C. *J Am Chem Soc* 2000, 122, 1830; (c) Komon, Z. J. A.; Diamond, G. M.; Leclerc, M. K.; Murphy, V.; Okazaki, M.; Bazan, G. C. *J Am Chem Soc* 2002, 124, 15280; (d) Komon, Z. J. A.; Bazan, G. C. *Macromol Rapid Commun* 2001, 22, 407; (e) Quijada, R.; Rojas, R.; Bazan, G. C. *Macromolecules* 2001, 34, 2411.
9. Kissin, Y. V.; Beach, D. L. *Stud Surf Sci Catal* 1986, 25, 231.
10. Barnhard, R. W.; Bazan, G. C.; Mourey, T. *J Am Chem Soc* 1998, 120, 1082.
11. Chien, J. C. W.; He, D. W. *J Polym Sci Polym Chem* 1991, 29, 1603.
12. Resconi, L.; Bossi, S.; Abis, L. *Macromolecules* 1992, 25, 3199.
13. Cheny, Y. X.; Marks, T. J. *Chem Rev* 2000, 100, 1391.
14. Koivumaki, J. *Polym Bull* 1996, 36, 7.
15. Linderman, L. P.; Adams, N. O. *Anal Chem* 1971, 43, 1245.
16. Galland, G. B.; Quijada, R.; Mauler, R. S.; de Menezes, S. C. *Macromol Rapid Commun* 1996, 17, 607.
17. Quijada, R. *Macromol Chem Phys* 1999, 200, 1306.