Living polymerization of 1,3-butadiene by a Ziegler–Natta type catalyst composed of iron(III) 2-ethylhexanoate, triisobutylaluminum and diethyl phosphite

Dirong Gong [a,b], Weimin Dong [a], Jinchang Hu [a], Xuequan Zhang [a,*], Liansheng Jiang [a]

[a] Laboratory of Polymer Engineering, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, PR China
[b] Graduate School of the Chinese Academy of Sciences, Beijing 100049, PR China

ARTICLE INFO

ABSTRACT

Living characteristics of facilely prepared Ziegler–Natta type catalyst system consisting of iron(III) 2-ethylhexanoate, triisobutylaluminum and diethyl phosphite have been found in the polymerization of 1,3-butadiene in hexane at 40 °C. The characteristics have been well demonstrated by: a first-order kinetics with respect to monomer conversion, a narrow molecular weight distribution ($M_w/M_n = 1.48$–1.52) of polybutadiene in the entire range of polymerization conversion and a good linearity between M_n and the yield of polymer. Feasible post-polymerization of 1,3-butadiene and block co-polymerization of 1,3-butadiene and isoprene further support the living natures of the catalyst bestowed with. The current catalyst system is highly active (yield $> 80\%$, 35 min), providing polybutadiene with 1,2, *cis*-1,4 and *trans*-1,4 units about 44.0%, 51.0% and 5.0%, respectively.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Living polymerization has attracted widespread attentions due to its feasibility to offer the polymer with controlled molecular weight and narrow molecular weight distribution, well-defined block copolymer as well as terminally functionalized materials [1,2]. Living radical polymerization, especially for polar monomers, has been gained such tremendous momentum [3–14] since Matyjaszewski [15] and Sawamoto [16] first reported two different catalyst systems independently in 1995. However, such systems have not been successfully extended for living polymerization of non-polar monomers, such as ethylene, isoprene and 1,3-butdiene [17–21]. Meanwhile, living anionic systems have been well developed for various monomers, particularly for polymerization of conjugated dienes, due to its strong background of practical applications [22–24].

Conventional Ziegler–Natta catalysts are claimed to be the powerful tools for promoting regio- and/or stereospecific polymerization of 1,3-butadiene at high levels, whereas the molecular weight distribution of polymer is fairly broad and the control of molecular weight is still very limited [25–29]. Some metallocene catalysts are characterized by precise controlling of molecular weight, molecular weight distribution and even the microstructure of polymer if conducting polymerization at the proper conditions [30–33]. Particularly, the catalyst systems developed by Cui [22] and Hou [34], which

show excellent living natures and high regio-selectivity (*cis*-1,4 $> 99\%$ and 3,4 $= 98\%$, respectively) even up to 80 °C in the polymerization of isoprene, though practical applications of the catalysts have not been demonstrated yet. Up to now, the catalyst systems for living polymerization of 1,3-butadiene are mainly limited to principally *cis*-1,4 dominated, those with much higher 1,2 selectivity have been far less studied, though high molecular weight 1,2-rich polybutadiene ($M_n > 10^5$) is a high-performance rubber having good wet-skid resistance and low rolling resistance [35,36] and that with low molecular weight ($M_n < 5 \times 10^4$) is widely utilized as adhesive, paint, crosslinking coagent and modifier. Most importantly, polarization of chain end by post-polymerization with polar compounds (PCl_3, $SnCl_4$, et al.) will broaden the applications of products.

In comparison of catalysts based on transition metals, such as vanadium, titanium, cobalt and neodymium, relatively few efforts had been devoted to iron-based catalysts because of low activity and poor regio-selectivity toward polymerization of 1,3-butadiene [37–42]. Though both activity and regio-selectivity have been substantially improved in the past decade [43–48], controlling of molecular weight is still a fascinating and challengeable subject in the area of 1,3-butadiene polymerization.

We have been interested in screening effective donors in iron-based catalysts for stereospecific polymerization of 1,3-butadiene. Easily prepared catalytic systems having good catalytic performances, such as high activity and controllable regio- and stereo-selectivity under mild polymerization conditions have been achieved [47,48]. Previously, we reported the catalyst system consisting of iron(III) 2-ethylhexanoate (Fe(2-EHA)$_3$), Al(i-Bu)$_3$ and

* Corresponding author. Tel./fax: +86 431 8526 2303.
  E-mail address: xqzhang@ciac.jl.cn (X. Zhang).

diethyl phosphite (DEP), is highly effective in 1,3-butadiene polymerization to produce 1,2-atactic polybutadiene and 1,2-syndiotactic polybutadiene. It should be mentioned that the active species derived from this catalyst system exhibit a distinguished tolerance to high temperature with comparison to that derived from catalysts with nitrogen contained compounds as donor, which are performed only at relatively low temperature [47]. In this paper, we report another promising nature of this catalyst system: the well demonstrated living characteristics toward polymerization of 1,3-butadiene. To our best knowledge, this is the first report concerning Ziegler–Natta type iron-based catalyst, with which the well molecular weight controlled polymerization of 1,3-butadiene is conducted, providing polybutadiene with medium 1,2-structure. These informative results shed light on the significance of donor in conventional Ziegler–Natta catalysts. Additionally, availability in controlling molecular weight by using this Ziegler–Natta type catalyst also gives a possibility in industrial applications.

2. Experimental

2.1. Materials

Fe(2-EHA)$_3$ was purchased from Alfa Aesar. Al(i-Bu)$_3$ was commercially available from AkzoNoble and diluted to 1.0 mol/L by hexane. Diethyl phosphite from Jinzhou Petrochemical Corporation, Petrochina, was distilled under reduced pressure. 1,3-Butadiene was also purchased from Jinzhou Petrochemical Corporation, Petrochina. Isoprene purchased from Fluka, was refluxed over calcium hydride for 2 h, distilled and stored under dry nitrogen. Hexane was dried by heating to reflux over sodium/diphenylketyl until the solution turned into blue and then distilled prior to use.

2.2. Polymerization procedure

All manipulations were carried out under a dry nitrogen atmosphere. A detailed polymerization procedure is described as a typical example. At first, a solution of 1,3-butadiene in hexane was prepared as the method described below: 1,3-butadiene was condensed into a vessel with volume grading, cooled at −10 °C and added via a bridge into the flask containing hexane. The 1,3-butadiene concentration was determined by weighing the vessel before charging it with hexane and after adding the 1,3-butadiene. The solution was divided via a distributor into portions and transferred to an oxygen and moisture free ampere bottle capped with a rubber plug. Catalyst components at desired molar ratio were consecutively injected into the ampoule in the sequence of Fe(2-EHA)$_3$, DEP and Al(i-Bu)$_3$ to induce polymerization at 40 °C. The polymerization was quenched after a given time by adding methanol containing 2,6-di-tert-butyl-4-methylphenol (1.0%) as a stabilizer. The polymer was washed with methanol repeatedly, cut into small pieces and finally dried in vacuum at 40 °C to constant weight. The polymer yield was determined by gravimetric analysis.

2.3. Polymer characterization

The number average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polymer were measured at 30 °C by gel permeation chromatography (GPC) equipped with a Waters 515 HPLC pump, four columns (HMW 7 THF, HMW 6E THF × 2, HMW 2 THF) and a Waters 2414 refractive index detector. Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL/min. The values of M_n and M_w/M_n were calculated by using polystyrene calibration. The microstructure of polymers was determined from ^{1}H NMR and ^{13}C NMR recorded on a Varian Unity 400 MHz spectrometer in CDCl$_3$ at room temperature and IR spectra measured
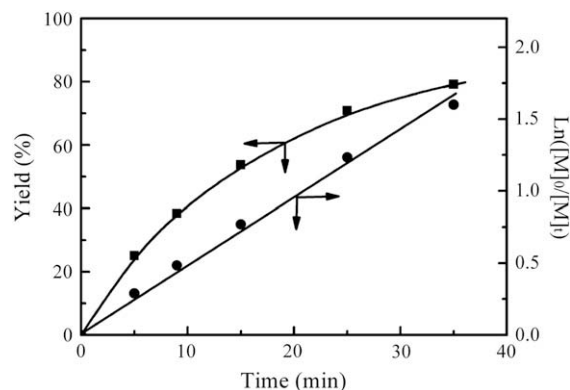

Fig. 1. Plots of yield and ln([M]$_0$/[M]$_t$) against polymerization time. Polymerization conditions: in hexane at 40 °C, [Bd] = 1.2 mol/L, [Bd]/[Fe] = 2000, [Al]/[Fe] = 6, [DEP]/[Fe] = 3.

with BRUKE Vertex-70 FIR spectrophotometer. The proportion of 1,2, *cis*-1,4 and *trans*-1,4 units of polymers were determined as reported in literatures [49–53].

3. Results and discussion

3.1. Homo-polymerization of 1,3-butadiene

Polymerization of 1,3-butadiene initiated by Fe(2-EHA)$_3$/Al(i-Bu)$_3$/DEP ([Bd]/[Fe] = 2000, [Al]/[Fe] = 6, [DEP]/[Fe] = 3) catalyst system was carried out at 40 °C in hexane. The yield, M_n and M_w/M_n of polymers at different polymerization time were determined and analyzed. Observed from the upper curve in Fig. 1, the rates of chain initiation and propagation are found to be fairly fast, polymer yield reaches about 80% in 35 min. Good linearity between ln[M]$_0$/[M]$_t$ ([M]$_0$ is the initial concentration of monomer, and [M]$_t$ stands for the monomer concentration at the stated time) and polymerization time is observed from the lower curve in Fig. 1, suggesting a first-order kinetics with respect to monomer conversion. It also indicates that the concentration of the living species remains constant during polymerization process, and irreversible chain termination reactions can be neglected [32,54]. The polybutadiene obtained at different time was analyzed by GPC. As shown in Fig. 2,
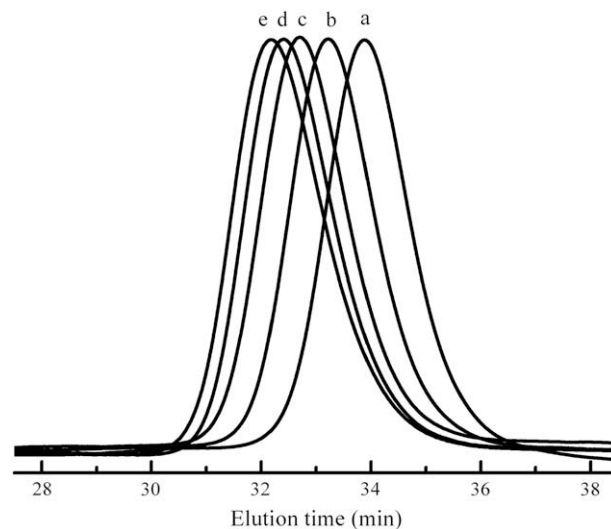

Fig. 2. Shift in GPC profiles of polymers obtained at different polymerization time: (a) 5 min (b) 9 min (c) 15 min (d) 25 min (e) 35 min. Polymerization conditions are the same as in Fig. 1.
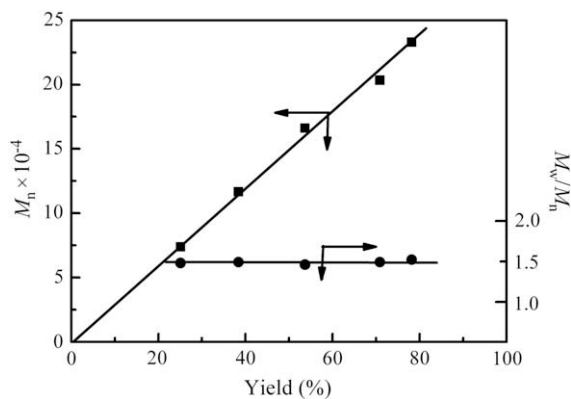
Fig. 3. Plots of M_n and M_w/M_n against polymer yield. Polymerization conditions are the same as in Fig. 1.

a monomodal and narrow GPC profile gradually shifts toward higher molecular weight region with time prolonging. Meanwhile, the values of M_w/M_n of the polymer keep around 1.5 throughout the polymerization process. The M_n of polymer is also plotted vs polymer yield (Fig. 3). The M_n of polymer increases linearly with the increase of polymer yield, and the line passes through the origin point, suggesting the absence of irreversible chain transfer reactions. The polybutadiene derived from this catalytic system possesses roughly constant microstructure with 1,2, cis-1,4, and trans-1,4 content in a ratio of 51.0:44.0:5.0 in the entire conversion range.

Presumably, coexistence of two types of active species, one producing 1,2 polybutadiene and the other producing cis-1,4 polybutadiene, seems to be a factor broadening the molecular weight distribution. With intent to investigate it's microstructure, ^{13}C NMR analysis of the polymer was carried out. As depicted in Fig. 4, the peaks at 25.8 and 33.5 ppm, can be unambiguously assigned to $-CH_2-$ in $-CH_2-CH=CH-CH_2-CH_2-CH(CH=CH_2)-$ and $-CH_2-CH=CH-CH_2-CH(CH=CH_2)-CH_2-$, respectively [50], implying that 1,2 and cis-1,4 units coexisted in one polymer chain, instead of in two separated chains. Additionally, the fact that only one T_g near −30 °C in the resulted polybutadiene was detected by DSC can exclude the mixtures of two types of polymer, cis-1,4 polybutadiene (T_g: −105 °C [54]) and 1,2 polybutadiene (T_g: 0–10 °C [55]) as well. Therefore, from this point, it is believed that
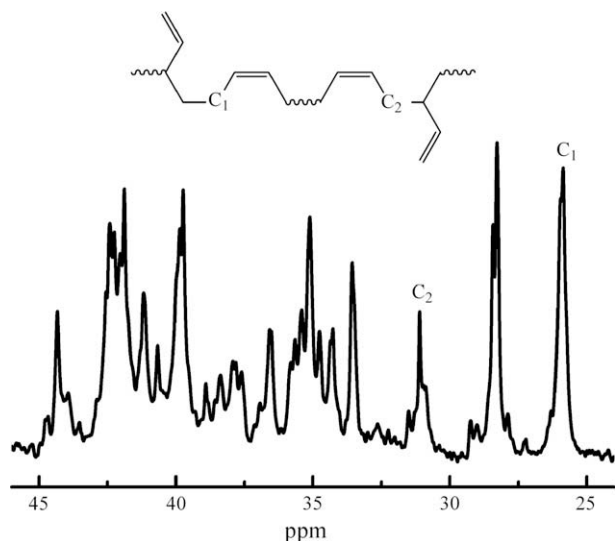

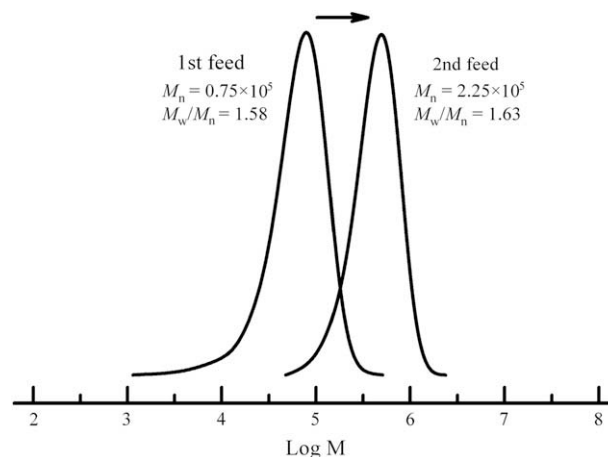Fig. 4. The aliphatic ^{13}C NMR of the obtained polybutadiene.

Fig. 5. GPC profiles of polymers obtained from two-step polymerization of 1,3-butadiene. Polymerization conditions: in hexane at 40 °C, $[Bd]_0 = 0.35$ mol/L, $[Bd]_0/[Fe] = 500$, $[Al]/[Fe] = 6$, $[DEP]/[Fe] = 3$, $[Bd]_{add} = 0.75$ mol/L, $[Bd]_{add}/[Fe] = 1080$.

polymerization was initiated by single active site, instead of multi-active sites. It is deducted that heterogeneity in microstructures (1,2 and 1,4-sequence distribution or/and the percentage of 1,2, cis-1,4 or trans-1,4 units) among the individual molecular chain is probably responsible for the broadened molecular weight distribution, as the Mark–Houwink constants of 1,2 and cis-1,4 polybutadiene are different.

3.2. Seeding polymerization of 1,3-butadiene

The living nature of the catalyst system is further examined by seeding polymerization. Two-step polymerizations of 1,3-butadiene were carried out. The first polymerization step ($[Bd]_0/[Fe] = 500$, $[Al]/[Fe] = 6$, $[DEP]/[Fe] = 3$) was completed within 1 h and yielded polybutadiene with a low molecular weight and narrow molecular weight distribution ($M_n = 0.75 \times 10^5$, $M_w/M_n = 1.58$). The catalyst system was left under 1,3-butadiene starved conditions for 8 h, then the second monomer feed ($[Bd]_{add}/[Fe] = 1080$, $[Bd]_{total}/[Fe] = 1580$) was added and the polymerization resumed smoothly, affording polybutadiene with a still narrow molecular weight distribution ($M_n = 2.25 \times 10^5$, $M_w/M_n = 1.63$) at total conversion about 95% after 1 h. Fig. 5 shows the GPC profiles of the polymers obtained from both polymerization stages, where
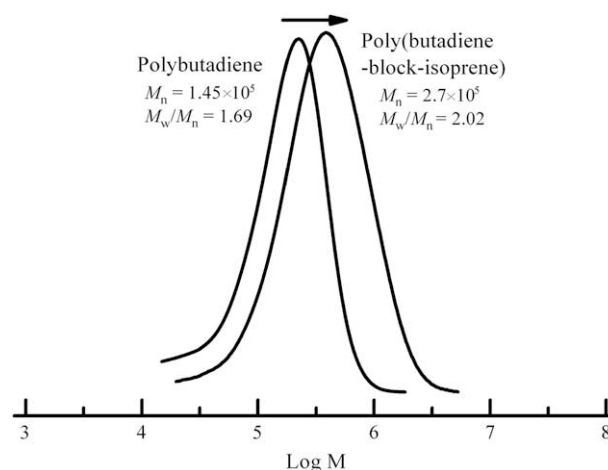

Fig. 6. GPC profiles of polybutadiene and poly(butadiene-block-isoprene). Polymerization conditions: in hexane at 40 °C, $[Bd]_0 = 0.35$ mol/L, $[Bd]_0/[Fe] = 1000$, $[Al]/[Fe] = 6$, $[DEP]/[Fe] = 3$, $[IP]_{add} = 0.30$ mol/L, $[IP]_{add}/[Fe] = 860$.
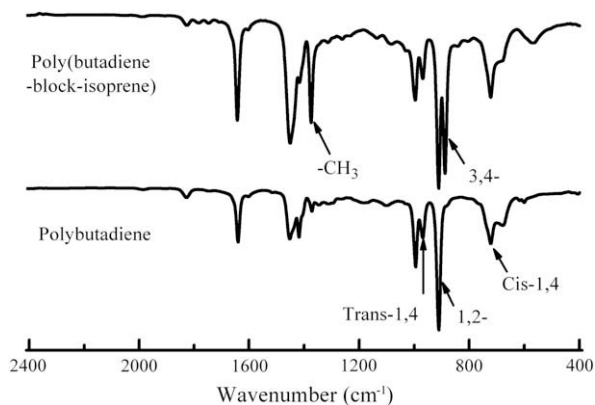
Fig. 7. IR spectra of polybutadiene and poly(butadiene-block-isoprene). Polymerization conditions are the same as in Fig. 6.

profile of the second stage polymer shifts to higher molecular weight region and maintains monomodal with almost the same molecular weight distribution.

3.3. Block co-polymerization of 1,3-butadiene and isoprene

The reactivity of the living end of polybutadiene toward isoprene monomer is also investigated. 1,3-Butadiene was polymerized ($[Bd]_0/[Fe] = 1000$, $[Al]/[Fe] = 6$, $[DEP]/[Fe] = 3$) until the monomer was completely consumed, producing a polybutadiene with M_n of 1.45×10^5 and M_w/M_n of 1.69 (Fig. 6), after 24 h, isoprene ($[IP]/[Bd] = 0.86$) was added to the reaction system for the second stage polymerization. The resulted poly(butadiene-block-isoprene) consists of polyisoprene segment of 40% with 3,4 units of 44%, 1,2 units of 12% and cis-1,4 units of 44% as determined from ^{1}H NMR. Fig. 7 shows the IR spectra of 1,3-butadiene homopolymer and poly(butadiene-block-isoprene) copolymer, where the new absorption peaks at 1374 cm^{-1} and 889 cm^{-1} (assigned to methyl groups and 3,4 units in polyisoprene, respectively) featured polyisoprene segment appears in the latter spectrum. The GPC curve of the copolymer shifts to a higher molecular weight region ($M_n = 2.70 \times 10^5$) with respect to that of the former 1,3-butadiene homopolymer and keeps monomodal with a slightly broadened molecular weight distribution ($M_w/M_n = 2.02$) as shown in Fig. 6. These results indicate the copolymer is not a mixed homopolymers but a true polybutadiene and polyisoprene block copolymer.

4. Conclusion

Living characteristics of Fe(2-EHA)$_3$/Al(i-Bu)$_3$/DEP catalyst system have been found in the polymerization of 1,3-butadiene. These characteristics have been well demonstrated by a narrow molecular weight distribution ($M_w/M_n \approx 1.5$) of the resulted polybutadiene and a linear relationship between $\ln[M]_0/[M]_t$ and polymerization time, number average molecular weight and polymer yield, respectively. Feasible post-polymerization of 1,3-butadiene, and block co-polymerization of 1,3-butadiene and isoprene verify the living natures. The obtained polybutadiene possesses 1,2 units of 51.0%, cis-1,4 of 44.0% and trans-1,4 of 5.0%. The controllable molecular weight by this facilely prepared catalyst with DEP as donor at a relative high temperature in hexane shows us the significant effects of donor on polymerization behaviors of Ziegler–Natta catalysts.

References

[1] Szwarc M, Levy M, Milkovich R. J Am Chem Soc 1956;78:2656–7.
[2] Risse W, Grubbs RH. Macromolecules 1989;22:1558–62.
[3] Goto A, Tsujii Y, Fukuda T. Polymer 2008;49:5177–85.
[4] Hou C, Qu RG, Sun CM, Ji CN, Wang CH, Ying L, et al. Polymer 2008;49:3424–7.
[5] Alam MN, Zetterlund PB, Okubo M. Polymer 2008;49:3428–35.
[6] Luo XX, Zhuang Y, Zhao X, Zhang M, Xu SS, Wang BQ. Polymer 2008;49:3457–61.
[7] Arita T, Kayama Y, Ohno K, Tsujii Y, Fukuda T. Polymer 2008;49:2426–9.
[8] Ting WH, Dai SA, Shih YF, Yang IK, Su WC, Jeng RJ. Polymer 2008;49:1497–505.
[9] Moad G, Rizzardo E, Thang SH. Polymer 2008;49:1079–131.
[10] Lutz JF, Schlaad H. Polymer 2008;49:817–24.
[11] Nicolas J, Ruzette AV, Farcet C, Gérard P, Magnet S, Charleux B. Polymer 2007;48:7029–40.
[12] Quinn JF, Davis TP, Barner L, Barner-Kowollik C. Polymer 2007;48:6467–80.
[13] Charleux B, Nicolas J. Polymer 2007;48:5813–33.
[14] Kahveci MU, Tasdelen MA, Yagci Y. Polymer 2007;48:2199–202.
[15] Wang JS, Matyjaszewski K. J Am Chem Soc 1995;117:5614–5.
[16] Kato M, Kamigaito M, Sawamoto M, Higashimura T. Macromolecules 1995;28:1721–3.
[17] Benoit D, Harth E, Fox P, Waymouth RM, Hawker CJ. Macromolecules 2000;33:363–70.
[18] Howell BA, Dineen MT, Kastl PE, Lyons JW, Meunier DM, Smith PB, et al. Macromolecules 1997;30:5194–9.
[19] Kobatake S, Harwood HJ, Quirk RP, Priddy DB. Macromolecules 1998;31:3735–9.
[20] Georges MK, Hamer GK, Listigovers NA. Macromolecules 1998;31:9087–9.
[21] Keoshkerian B, Georges MK, Quinlan M, Veregin R, Goodbrand B. Macromolecules 1998;31:7559–61.
[22] Wang BL, Cui DM, Lv K. Macromolecules 2008;41:1983–8.
[23] Jiang LS, Dong WM, Zhang XQ. U.S. Patent 7, 288611; 2007.
[24] Luo S. U.S. Patent 6,528,588 B2; 2003.
[25] Ji XZ, Pan SF, Li YL, Ouyang J. Sci Sin B 1985;2:120–7.
[26] Nath DCD, Shiono T, Ikeda T. Macromol Chem Phys 2000;203:756–60.
[27] Endo K, Hatakeyama N. J Polym Sci Part A Polym Chem 2001;39:2793–8.
[28] Hadjiandreous P, Julemont M, Teryssie P. Macromolecules 1984;17:2455–6.
[29] Deming TJ, Novak BM, Ziller JW. J Am Chem Soc 1994;116:2366–74.
[30] Miyazawa A, Kase T, Soga K. Macromolecules 2000;33:2796–800.
[31] Miyazawa A, Kase T, Hashimoto K. Macromolecules 2004;37:8840–5.
[32] Kaita S, Hou ZM, Wakatsuki Y. Macromolecules 1999;32:9078–9.
[33] Kaita S, Hou ZM, Wakatsuki Y. Macromolecules 2001;34:1539–41.
[34] Zhang LX, Suzuki T, Luo Y, Nishiura M, Hou ZM. Angew Chem Int Ed 2007;46:1909–13.
[35] Schuring DJ, Futamura S. Rubber Chem Tech 1990;63:315–67.
[36] Yoshioka H, Komura K, Watanabe H, Akita S, Masuda T, Nakajima A. Pure Appl Chem 1986;58:1697–706.
[37] Cao LH, Dong WM, Jiang LS, Zhang XQ. Polymer 2007;48:2475–80.
[38] Ren CY, Li GL, Dong WM, Jiang LS, Zhang XQ, Wang FS. Polymer 2007;48:2470–4.
[39] Dong WM, Masuda T. J Polym Sci Part A Polym Chem 2002;40:1838–44.
[40] Dong WM, Endo K, Masuda T. Macromol Chem Phys 2003;204:104–10.
[41] Swift HE, Bozik JE, Wu CY. J Catal 1970;17:331–40.
[42] Zhang ZY, Zhang HJ, Ma HM, Wu Y. J Mol Catal 1982;17:65–76.
[43] Nakayama Y, Baba Y, Yasuda H, Kawakita K, Ueyama N. Macromolecules 2003;36:7953–8.
[44] Bazzini C, Giarrusso A, Porri L. Macromol Rapid Commun 2002;23:922–7.
[45] Ricci G, Morganti D, Sommazzi A, Santi R, Masi F. J Mol Catal A: Chemical 2003;204–205:287–93.
[46] Luo S. U.S.Patent 6,284,702; 2001.
[47] Lu J, Hu YM, Zhang XQ, Bi JF, Dong WM, Jiang LS, et al. J Appl Polym Sci 2006;100:4265–9.
[48] Hu YM, Dong WM, Jiang LS, Zhang XQ, Guo Y, Cao LH. Chin J Catal 2005;8:664–8.
[49] Elgert KF, Quack G, Stutzel B. Polymer 1974;15:612–3.
[50] Elgert KF, Quack G, Stutzel B. Polymer 1974;15:816–8.
[51] Elgert KF, Quack G, Stutzel B. Polymer 1975;16:154–6.
[52] Ricci G, Forni A, Boglia A, Sonzogni M. Organometallics 2004;23:3727–32.
[53] Yu BS. Chin J Anal Chem 1974;2:311–4.
[54] Friebe L, Nuyken O, Obrecht W. Adv Polym Sci 2006;204:1–154.
[55] Dolgoplosk BA, Tinyakova EI. Polymer Sci, Ser A 1994;36:1380–403.