



Polymerization of 1,3-butadiene catalyzed by a thermal robust, high selective and active iron catalyst: An applicable recipe for producing syndiotactic 1,2-polybutadiene



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ABSTRACT

A novel class of organic phosphates were synthesized and applied in iron catalyst as additive for 1,2-syndiotactic polymerization of 1,3-butadiene in combination with aluminum alkyls ($\text{Al}^i\text{-Bu}_3$ or AlEt_3) in hexane at industrial favorable 50–100 °C. Remarkable enhanced polymer productivity (up to 486 kg (polymer)/mol(Fe) h) and excellent 1,2-syndiotactic regularity have been achieved at 50–100 °C in all examining cases. All the polymers obtained under various polymerization conditions possess prevalingly 1,2 inserted homo-sequences up to 94.7% 1,2-selectivity in syndiotactic arrangements (up to 94.4%, denoted by *rrrr*) with melting point ranging from 170 to 182 °C. The current in-situ generated catalyst systems feature high productivity, selectivity, robustness (e.g. high thermal stability, good tolerance to poisons and environmentally friendly hexane as solution polymerization medium) and single-site behaviour. These all extend the practical usefulness of these versatile phosphates assisted catalyst, and they are promising candidates to act as ancillary additive for industrial applicable 1,2-syndiotactic polymerization of 1,3-butadiene.

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1. Introduction

The polymerization of 1,3-conjugated dienes is one of the most important industrial processes, as it affords efficient entries toward rubber materials with versatile properties for a wide range of applications. The effective control of chain structure, e.g. regio-and/or stereoselectivity of polydiene are of prime importance because these chemical structures are crucial to the resultant polymer properties. In particular, 1,3-butadiene is an attractive monomer and its stereospecific polymerization affords polybutadienes with diversified microstructures (i.e., 1,4-*cis* [1–9], 1,4-*trans* [10–21], 1,2-syndiotactic [22–31] and 1,2-atactic [32,33] as well as their combinations [32–34]. Following Natta's pioneering study in the 1960s

[10], numerous metal catalysts have been exploited for the selective polymerization of 1,3-butadiene, especially *cis*-1,4 selective polymerization, whereas, 1,2-polymerization is less developed, probably due to the limited understanding of the catalysis process and catalyst structure-polymer properties relationship, although the product 1,2-polybutadiene, depending on the stereoregularity, have been used to manufacture tire, sole, preservative film as well as filler as reinforcing agent.

Conventional Ziegler–Natta catalysts are known to be the powerful tools for promoting regio- and/or stereospecific polymerization of 1,3-butadiene at high levels and currently the only type for industrial production of 1,2-syndiotactic polybutadiene. For the current only two applicable 1,2-selective systems $\text{Co}(\text{acac})_3/\text{AlEt}_3/\text{CS}_2$ [35] or $\text{Co}(\text{acac})_2/\text{AlEt}_3/\text{H}_2\text{O}/\text{PPh}_3$ (in dichloromethane medium) [36,37], the use of halide solvent or smelling CS_2 additive have raised a serial environmental (toxic !) and safety (inflammable !) issues. Additionally, the high crystallinity and melting points (>200 °C) of the resultant polymers have led to polymer processing rather energy consuming along with an increasing risk of thermal

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crosslinking. Therefore, it is of significant industrial importance to explore potential catalyst for production of 1,2-polybutadiene with improved properties under mild polymerization conditions. Recently, 1,2-stereoselective control of polybutadiene has been reported by Ricci and coworkers [30,38,39] using chromium and cobalt complexes ligated with phosphine ligand, however, the tedious synthetic procedures with associated high cost of catalyst components and low catalytic productivity could present some challenges for practical application.

We have been focusing on developing Ziegler-Natta type iron catalysts for production of stereoregular polybutadiene. The advantages of this attractive benign-metal catalysts surrogate stem from two considerations: (1) the ease of preparation (readily available and/or high thermal and chemical stability of catalyst components) and easy handling of catalyst components, (2) the use of low-cost, innocuous, and earth abundant metal with biocompatibility and negligible environmental impact. Despite interest in the development of new iron catalytic systems, the iron catalyst has a long remained challenge for polymer chemists due to their poor reactivity and regio/stereoselectivity issues associated to their diene polymerization [40–42]. The activity has been improved by introducing bidentate and tridentate donor (ligand) [43–45], but the ability to the high selective polymerization is still limited, particularly at higher polymerization temperature, for example, high selectivity (1,2-selectivity: 91%) is achievable only at $-78\text{ }^{\circ}\text{C}$ compromised by a low polymer yield (cal. 20%), which can be improved at $50\text{ }^{\circ}\text{C}$ along with sacrificing selectivity [44]. Recent discoveries have suggested that there may be a surprising advantage to using commercial available phospho(i)te as third component for improving both selectivity and activity, and thus has offered a range of potential industrially relevant catalyst components, which are more forgiving in terms of easy synthetic feasibility, cost and labour intensity, yet still deliver excellent control over the stereoregularity of the polymer with satisfied catalytic activity. Quest for such additives has advanced recently with development of dialkylphosphite, with which the iron catalyst produced 1,2-enriched polybutadiene possessing syndio arrangements (1,2-selectivity: 87–95%, pentad *rrrr* denoted syndio-tacticity: 81–90%), atactic 1,2-polybutadiene (as elastomer, 1,2-: 55–87%) as well as their block copolymer and in-situ formed blend by controlling the activators feeding at industrially favored polymerization conditions [32,33,46,47]. These exceptional findings stimulated our interest in continuing innovation of potential additive for increasing the catalytic properties, e.g. catalytic productivity, regio/stereoselectivity and thermal stability, in this manuscript we describe the synthesis of a new type of phospho(i)te compounds and their roles as additives in iron catalyst for stereoselective polymerization of 1,3-butadiene. The additive dependent catalytic performances have been investigated by varying the nature of phosphate, and the mechanism on how the phosphate assisted iron catalyst promoted such high 1,2-regio and stereoselectivity has also been proposed.

2. Experimental

2.1. General methods

Iron(III) acetylacetonate ($\text{Fe}(\text{acac})_3$), phosphorus(V) oxychloride, phenyl phosphorodichloridate and diphenylphosphorochloridate, tri-*tert*-butylaluminum (Al^iBu_3 (TIBA), 1.0 mol/L in hexane), *m*-dihydroxybenzene, 2,6-dihydroxypyridine, 2-methylpropane-1,3-diol, 2-hydroxypyridine were all purchased from Aldrich. Polymerization-grade 1,3-butadiene was also supplied from Aldrich and purified by passing through columns packed with 4 Å and KOH prior to use. All solvents used were purified in the

standard manner. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{31}P NMR (162 MHz) were recorded on a Bruker spectrometer at room temperature for organic donor in CDCl_3 and polymers in $o\text{-C}_6\text{D}_4\text{Cl}_2$ at $125\text{ }^{\circ}\text{C}$ for syndiotactic polymers. FT-IR data were collected on the BRUKE VERTEX-70 spectrophotometer. DSC measurements were performed on a Perkin-Elmer Diamond differential scanning calorimeter at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$, and the crystallinity were estimated referred to standard enthalpy of 1,2-PBD with 100% crystallinity. MS spectral was performed at THERMO SCIENTIFIC ACELA-LCQ Fleet. The number-average molecular weight (M_n) and the polydispersity index of polymer samples (M_w/M_n) were determined at $125\text{ }^{\circ}\text{C}$ by a PL-GPC 220 type high-temperature chromatograph equipped with three Plgel 10 lm Mixed-B LS type columns. 1,2,4-Trichlorobenzene was used as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL-Ltd.). The proportion of 1,2, *cis*-1,4 and *trans*-1,4 units of polymer were determined as reported literature.

2.2. Synthesis and characterization of additive

Phosphates were all prepared following the previously reported procedure (NMR spectrum were attached in the supporting information, Fig.1s–18s).

2.2.1. Diphenyl 3,5-dimethyl-1H-pyrazol-1-yl-1-phosphonate (P1)

^1H NMR (400 MHz, CDCl_3 , ppm): 7.25–7.21 (m, 10H, H_{ph}), 5.94 (s, 1H, H_{pz} , $^4J_{\text{P-H}} = 4.4\text{ Hz}$), 2.35 (s, 3H, $-\text{CH}_3$), 2.29 (s, 3H, $-\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3 , ppm): 154.90 (d, $C_{\text{pz-3}}$, $^3J_{\text{P-C}} = 14.6\text{ Hz}$), 149.84 (d, $C_{\text{ph-1}}$, $^2J_{\text{P-C}} = 6.5\text{ Hz}$), 148.33 (d, $C_{\text{pz-5}}$, $^2J_{\text{P-C}} = 13.1\text{ Hz}$), 129.79 ($C_{\text{ph-3}}$), 125.82 ($C_{\text{ph-4}}$), 120.62 (d, $C_{\text{ph-2}}$, $^3J_{\text{P-C}} = 4.7\text{ Hz}$), 109.80 (d, $C_{\text{pz-4}}$, $^3J_{\text{P-C}} = 9.3\text{ Hz}$), 13.83 ($-\text{CH}_3$), 12.83 ($-\text{CH}_3$). ^{31}P NMR (162 MHz, CDCl_3 , ppm): -15.05 . EI-MS for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_3\text{P}$ (m/z): 328 ($\text{M}+\text{Na}^+$).

2.2.2. Phenyl di-(3,5-dimethyl-1H-pyrazol-1-yl-1-)phosphonate (P2)

^1H NMR (400 MHz, CDCl_3 , ppm): 7.37–7.21 (m, 5H, H_{ph}), 5.97 (s, 2H, H_{pz} , $^4J_{\text{P-H}} = 4.2\text{ Hz}$), 2.51 (s, 6H, $-\text{CH}_3$), 2.27 (s, 6H, $-\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3 , ppm): 154.85 (d, $C_{\text{pz-3}}$, $^3J_{\text{P-C}} = 15.3\text{ Hz}$), 149.45 (d, $C_{\text{ph-1}}$, $^2J_{\text{P-C}} = 7.0\text{ Hz}$), 147.88 (d, $C_{\text{pz-5}}$, $^2J_{\text{P-C}} = 12.3\text{ Hz}$), 129.78 ($C_{\text{ph-3}}$), 125.98 ($C_{\text{ph-4}}$), 120.98 (d, $C_{\text{ph-2}}$, $^3J_{\text{P-C}} = 4.7\text{ Hz}$), 110.34 (d, $C_{\text{pz-4}}$, $^3J_{\text{P-C}} = 8.7\text{ Hz}$), 13.87 ($-\text{CH}_3$), 12.92 ($-\text{CH}_3$). ^{31}P NMR (162 MHz, CDCl_3 , ppm): -13.05 . EI-MS for $\text{C}_{16}\text{H}_{19}\text{N}_4\text{O}_2\text{P}$ (m/z): 330 ($\text{M}+\text{Na}^+$).

2.2.3. Tris(3,5-dimethylpyrazolyl)phosphine oxide (P3)

^1H NMR (600 MHz, CDCl_3 , ppm): 6.00 (s, 3H, H_{pz} , $^4J_{\text{P-H}} = 2.5\text{ Hz}$), 2.29 (s, 9H, $-\text{CH}_3$), 2.18 (s, 9H, $-\text{CH}_3$). ^{13}C NMR (125 MHz, CDCl_3 , ppm): 154.50 (d, $C_{\text{pz-3}}$, $^3J_{\text{P-C}} = 15.7\text{ Hz}$), 147.68 (d, $C_{\text{pz-5}}$, $^2J_{\text{P-C}} = 12.1\text{ Hz}$), 110.66 (d, $C_{\text{pz-4}}$, $^3J_{\text{P-C}} = 8.1\text{ Hz}$), 13.60 ($-\text{CH}_3$), 11.93 ($-\text{CH}_3$). ^{31}P NMR (242 MHz, CDCl_3 , ppm): -10.77 . EI-MS for $\text{C}_{15}\text{H}_{21}\text{N}_6\text{PO}$ (m/z): 332 ($\text{M}+\text{Na}^+$).

2.2.4. 1,3-(Diphenyl phosphate)-2-methylpropane (P4)

^1H NMR (400 MHz, CDCl_3 , ppm): 7.32–7.24 (m, 8H, H_{ph}), 7.23–7.16 (m, 12H, H_{ph}), 4.21 (dd, 4H, $-\text{CH}_2-$), 2.23 (m, 1H, $-\text{CH}(\text{CH}_3)-$), 0.97 (d, 3H, $-\text{CH}_3$, $J = 5.1\text{ Hz}$). ^{13}C NMR (100 MHz, CDCl_3 , ppm): 150.45 (C_{ph}), 129.87 (C_{ph}), 125.48 (C_{ph}), 120.06 (C_{ph}), 69.43 ($-\text{CH}_2-$), 34.93 ($-\text{CH}-$), 12.79 ($-\text{CH}_3$). ^{31}P NMR (162 MHz, CDCl_3 , ppm): -12.04 . EI-MS for $\text{C}_{28}\text{H}_{28}\text{P}_2\text{O}_8$ (m/z): 577 ($\text{M}+\text{Na}^+$).

2.2.5. 1,3-(Diphenyl phosphate)benzene (P5)

^1H NMR (400 MHz, CDCl_3 , ppm): 7.35–7.33 (m, 10H, H_{ph}), 7.24–7.15 (m, 12H, H_{ph}). ^{13}C NMR (100 MHz, CDCl_3 , ppm): 151.03 (C_{ph}), 150.33 (C_{ph}), 130.73 (C_{ph}), 129.96 (C_{ph}), 125.46 (C_{ph}), 120.72

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