



Syndiotactically enriched 1,2-selective polymerization of 1,3-butadiene initiated by iron catalysts based on a new class of donors

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ABSTRACT

A series of phosphoryl (P=O) contained compounds: triethylphosphate (**a**), diethylphenylphosphate (**b**), ethyldiphenylphosphate (**c**) triarylphosphates (**d** and **h–m**), triphenylphosphine oxide (**e**), phenyl diphenylphosphinate (**f**) and diphenyl phenylphosphonate (**g**) have been prepared. Iron catalysts, which are generated *in situ* by mixing the compounds with Fe(2-EHA)₃ and AlⁱBu₃ in hexane, are tested for butadiene polymerization at 50 °C. Phosphates donated catalysts have been, unprecedentedly, found to conduct extremely high syndiotactically (pentad, *rrrr* = 46.1–94.5%) enriched 1,2-selective (1,2-structure content = 56.2–94.3%) polymerization of butadiene. Introduction of electron withdrawing substituents on phenyl rings of triphenylphosphate (**k–m**) remarkably promotes catalytic activity, while bulky substituent isopropyl at 2-position (**h**) has beneficial influence on regioselectivity. Employment of **e**, **f** or **g** as donor, results in a suppressed monomer conversion, accompanied by deteriorated 1,2-regioselectivity. The effects of polymerization conditions such as reaction temperature, types of cocatalysts and polymerization medium are also investigated by using catalyst system with tri(2,4-difluorophenyl)phosphate (**m**) as donor. Highly tolerance to polymerization temperature up to 80 °C is observed for the first time in the iron-based catalyst.

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1. Introduction

Regio- and/or stereospecific polymerizations of butadiene are of great interests and importance from viewpoints of polymers design and their applications as polymer materials. It is well known that the development of catalysts has been the key factor in evolution of regio- and/or stereospecific polymerization of butadiene. Catalysts based on various metals including titanium, cobalt, nickel, and lanthanide metal complexes in the presence of MAO, aluminum alkyls or aluminum alkyls/borate provide high *cis*-1,4 selectivity for the polymerization of butadiene to afford the most important synthetic rubber [1]. In the meanwhile, the interests in *trans*-1,4 polybutadiene has emerged in rubber and tire industries; thus, a large number of catalyst systems have been explored to provide *trans*-1,4-selectivity [2]. To date, catalyst systems for preparing 1,2-rich polybutadienes have not been explored as extensively as those for *cis*-1,4 polymer [3], even though these materials are commercial important either as rubber where the vinyl groups as side chains are randomly placed on the sides with respect to the polymer main chain or as thermoplastic where the groups are alternately

positioned on the opposite sides. Recently, cobalt and chromium-based systems, such as CoCl₂(PPh_xR_{3-x})₂/MAO (R = Me, Et, ⁱPr, et al. x = 1, 2 or 3) [3h] Co(2-EHA)₂/AlEt₃/H₂O/Ph₃P [3i] and CrCl₂(P(OP)₂ (bidentate phosphine ligand)/MAO [3j,3k] have been mainly reported for 1,2-specific polymerization of butadiene. With regard to iron catalysts, previous investigations are focused on searching for donors such as anilines, 1,10-phenanthroline and azodiisobutyronitrile to improve catalytic activity and 1,2-selectivity [4], but little improvement has been achieved. Hopefully, progress has been made by using FeCl₂(bipy)₂/MAO (1,2-units: 91%, syndiotacticity, denoted by *rrrr*: 52.5%, polymerization conditions: at –78 °C for about 3 days) [5] and FeEt₂(bipy)₂/MAO (weakly crystalline 1,2-polybutadiene, polymerization conditions: at 0 °C or below) [6]. In spite of the recent improvement, the aforementioned emerging systems are fascinating merely in academic fields, complicated catalyst preparation, aromatic medium used or low activity suffered in some cases are the primary reasons diminishing the possible applications. Though two catalyst systems Co(acac)₃/AlEt₃/CS₂ [7] and Co(acac)₂/AlEt₃/H₂O/PPH₃ (halogenated solvent as polymerization medium) [8], have been industrialized for the syndiotactically 1,2-polymerization of butadiene, in want of perfection, either obnoxious CS₂ or toxic halogenated solvent has adverse environmental impacts. Therefore, further exploration of new catalyst systems, having high activity, high regio- as well as

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stereoselectivity under mild polymerization conditions, is still a challengeable and attractive subject from both academic and industrial fields.

The discovery of dialkylphosphites as effective donors in iron-based catalysts for syndiotactically 1,2-polymerization of butadiene has renewed interest in new donor over the past decade [9]. Inspired by the promising results investigated in our groups, our subsequent exploration involves a new type of P=O contained compounds as donor in iron catalyst to probe the effect that subtle modifications to the structure of donor have on catalytic performance. Screening results show high monomer conversion and high 1,2-syndiotactic stereospecificity can be simultaneously achieved by employing phosphate as donor. The influence of polymerization temperature, types of cocatalysts and polymerization medium are also investigated. Sharply contrast to those above mentioned iron catalysts [4–6], the current system exhibits excellent tolerance towards high polymerization temperature up to 80 °C. The high catalytic activity and 1,2-syndioselectivity under the mild polymerization conditions (in hexane, at 50 °C) furnish a possibility in industrial applications.

2. Experimental

2.1. Materials

Phenols were purchased from Aldrich. Triethylphosphate and triphenylphosphine oxide were purchased from Acros Chemicals. Iron(III) 2-ethylhexonate (Fe(2-EHA)₃) (Fe(2-EHA)₃ in mineral spirits, 54.0 wt%), diphenylphosphinic chloride, phenylphosphonic dichloride, phosphorus(V) oxychloride, phenyl phosphorodichloridate and diphenyl phosphorochloridate were all purchased from Alfa Aesar. AlⁱBu₃ was commercially available from Akzo-Noble, and diluted to 1.0 mol/L solution by hexane. Polymerization-grade butadiene was supplied from Jinzhou Petrochemical Corporation and purified by passing through four columns packed with 4 Å and KOH before use. All solvents used were purified in the standard manner.

2.2. Synthesis and characterization of phosphoryl contained compounds

Diethylphenylphosphate (**b**), ethyldiphenylphosphate (**c**) phenyl diphenylphosphinate (**f**) and diphenyl phenylphosphonate (**g**) were prepared as reported methods [10,11].

Triphenylphosphate was synthesized with the following method (Scheme 1). To a mixture of phenol (3.1 g, 3.3 mmol) and sodium hydroxide (0.14 g, 3.5 mmol), a solution of phosphorus(V) oxychloride (1.54 g, 1.0 mmol) in toluene (30 mL) was

slowly added under vigorous stirring. The reaction mixture was stirred for 3 h, and a solution of NaOH (5.0 g) in water (30 mL) was added. The organic layer was separated and the aqueous layer was extracted with 3 × 15 mL of toluene. The combined organic extracts were washed with saturated brine (3 × 15 mL), and dried by anhydrous Na₂SO₄ overnight. Toluene was removed under the reduced pressure, and the final product was recrystallized from ethanol, affording **d** as a white solid (2.47 g, 76%). Compounds (**h–m**) were obtained following the similar procedure.

Diethylphenylphosphate (b) Yield: 71%. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.34–7.31 (m, 2H, Ph-H), 7.23–7.21 (m, 2H, Ph-H), 7.19–7.17 (m, 1H, Ph-H), 4.22 (q, 4H, J = 6.40 Hz, –CH₂CH₃), 1.35 (t, 6H, J = 6.40 Hz, –CH₂CH₃). ³¹P NMR (162 MHz, CDCl₃, δ, ppm): –6.69. IR (KBr, cm⁻¹): 3071, 3034, 1278 (ν_{P=O}), 1040, 1027, 959 (ν_{P–OPh}). Anal. Calcd. For C₁₀H₁₅PO₄: C, 52.18; H, 6.57. Found: C, 52.00; H, 6.76.

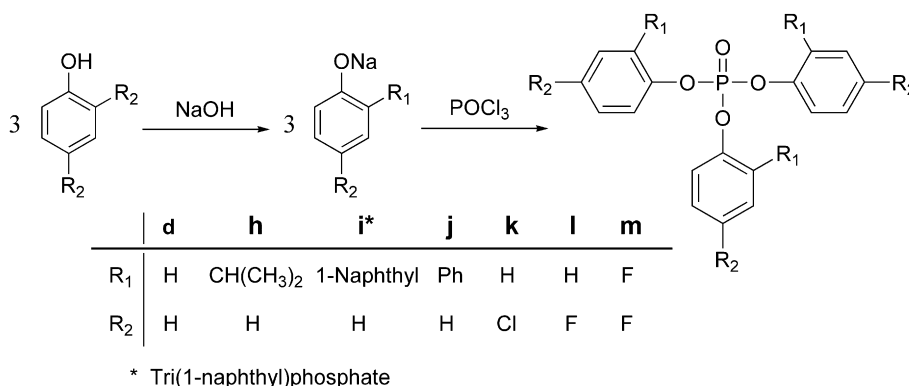
Ethyldiphenylphosphate (c) Yield: 51%. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.02–7.00 (m, 4H, Ph-H), 6.97–6.95 (m, 4H, Ph-H), 6.90–6.87 (m, 2H, Ph-H), 4.03 (q, 2H, J = 7.20 Hz, –CH₂CH₃), 1.06 (t, 3H, J = 7.20 Hz, –CH₂CH₃). ³¹P NMR (162 MHz, CDCl₃, δ, ppm): –12.17. IR (KBr, cm⁻¹): 3071, 3045, 1292 (ν_{P=O}), 1041, 1009, 952 (ν_{P–OPh}). Anal. Calcd. For C₁₄H₁₅PO₄: C, 60.43; H, 5.43. Found: C, 60.58; H, 5.31.

Triphenylphosphate (d) Yield: 86%. mp: 53–49 °C. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.37–7.32 (m, 6H, Ph-H), 7.28–7.25 (m, 3H, Ph-H), 7.23–7.18 (m, 6H, Ph-H). ³¹P NMR (162 MHz, CDCl₃, δ, ppm): –17.99. IR (KBr, cm⁻¹): 3098, 3060, 3019, 1295 (ν_{P=O}), 1030, 1010, 953 (ν_{P–OPh}). Anal. Calcd. For C₁₈H₁₅PO₄: C, 66.26; H, 4.63. Found: C, 66.41; H, 4.78.

Phenyl diphenylphosphinate (f) Yield: 76%. mp: 139–143 °C. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.92–7.87 (m, 4H Ph-H), 7.56–7.52 (m, 2H, Ph-H), 7.48–7.43 (m, 4H, Ph-H), 7.24–7.19 (m, 4H, Ph-H), 7.09–7.06 (m, 1H, Ph-H). ³¹P NMR (162 MHz, CDCl₃, δ, ppm): 30.02. IR (KBr, cm⁻¹): 3095, 3053, 3028, 1440 (ν_{P–Ph}), 1223 (ν_{P=O}), 1027, 998 (ν_{P–OPh}). Anal. Calcd. For C₁₈H₁₅PO₂: C, 73.46; H, 5.14. Found: C, 72.32; H, 5.05.

Diphenyl phenylphosphonate (g) Yield: 85%. mp: 71–76 °C. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.99–7.94 (m, 2H, Ph-H), 7.62–7.58 (m, 1H, Ph-H), 7.52–7.48 (m, 2H, Ph-H), 7.31–7.27 (m, 5H, Ph-H), 7.20–7.12 (m, 5H, Ph-H). ³¹P NMR (162 MHz, CDCl₃, δ, ppm): 11.37. IR (KBr, cm⁻¹): 3094, 3054, 3025, 1445 (ν_{P–OPh}), 1264 (ν_{P=O}), 1024, 1008, 969 (ν_{P–OPh}). Anal. Calcd. For C₁₈H₁₅PO₃: C, 69.68; H, 4.87. Found: C, 69.64; H, 4.52.

Tri(2-iso-propylphenyl)phosphate (h) Yield: 69%. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.35–7.15 (m, 12H, Ph-H), 2.88 (hept, 3H, J = 4.00 Hz, –CH(CH₃)₂), 1.12 (d, 18H, J = 4.00 Hz, –CH(CH₃)₂). ³¹P NMR (162 MHz, CDCl₃, δ, ppm): –17.97. IR (KBr, cm⁻¹): 3074, 3045, 1300 (ν_{P=O}), 1026, 1010, 956 (ν_{P–OPh}). Anal. Calcd. For C₂₇H₃₃PO₄: C, 71.66; H, 7.35. Found: C, 71.81; H, 7.22.



Scheme 1. Synthesis of triphenylphosphate derivatives.

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