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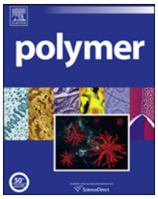

Syndiotactically enriched 1,2-selective polymerization of 1,3-butadiene initiated by iron catalysts based on a new class of donors

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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 $Fe(2\text{-}EHA)_3$ and $Al^{i}Bu_3$ in hexane, are tested for butadiene polymerization at 50 °C. Phosphates donated catalysts have been, unprecedently, 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.

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 $CoCl_2(PPh_xR_{3-x})_2/MAO$ (R = Me, Et, ^{i}Pr, et al. $x = 1$, 2 or 3) [3h] $Co(2\text{-}EHA)_2/AlEt_3/H_2O/Ph_3P$ [3i] and $CrCl_2(P\cap P)_2$ (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-phenantroline and azodiisobutyronitrile to improve catalytic activity and 1,2-selectivity [4], but little improvement has been achieved. Hopefully, progress has been made by using $FeCl_2(bipy)_2/MAO$ (1,2-units: 91%, syndiotacticity, denoted by *rrrr*: 52.5%, polymerization conditions: at −78 °C for about 3 days) [5] and $FeEt_2(bipy)_2/MAO$ (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 $Co(acac)_3/AlEt_3/CS_2$ [7] and $Co(acac)_2/AlEt_3/H_2O/PPh_3$ (halogenated solvent as polymerization medium) [8], have been industrialized for the syndiotactically 1,2-polymerization of butadiene, in want of perfection, either obnoxious CS_2 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. Al^{i}Bu$_3$ 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 Na$_2$SO$_4$ 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%. ^{1}H NMR (400 MHz, CDCl$_3$, 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, –CH_2CH$_3$), 1.35 (t, 6H, $J = 6.40$ Hz, –CH$_2$CH_3). ^{31}P NMR (162 MHz, CDCl$_3$, δ, ppm): −6.69. IR (KBr, cm^{-1}): 3071, 3034, 1278 ($\nu_{\mathrm{P=O}}$), 1040, 1027, 959 ($\nu_{\mathrm{P-OPh}}$). Anal. Calcd. For C$_{10}$H$_{15}$PO$_4$: C, 52.18; H, 6.57. Found: C, 52.00; H, 6.76.

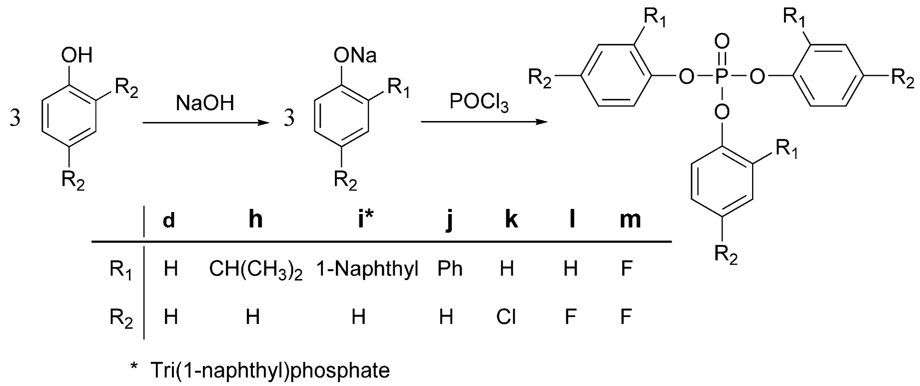
*Ethyldiphenylphosphate (**c**)* Yield: 51%. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 7.02–7.00 (m, 4H, Ph-*H*), 6.97–6.95 (m, 4H, Ph-*H*), 6.90–6.87 (m, 2H, Ph-*H*), 4.03 (q, 2H, $J = 7.20$ Hz, –CH_2CH$_3$), 1.06 (t, 3H, $J = 7.20$ Hz, –CH$_2$CH_3). ^{31}P NMR (162 MHz, CDCl$_3$, δ, ppm): −12.17. IR (KBr, cm^{-1}): 3071, 3045, 1292 ($\nu_{\mathrm{P=O}}$), 1041, 1009, 952 ($\nu_{\mathrm{P-OPh}}$). Anal. Calcd. For C$_{14}$H$_{15}$PO$_4$: C, 60.43; H, 5.43. Found: C, 60.58; H, 5.31.

*Triphenylphosphate (**d**)* Yield: 86%. mp: 53–49 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 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*). ^{31}P NMR (162 MHz, CDCl$_3$, δ, ppm): −17.99. IR (KBr, cm^{-1}): 3098, 3060, 3019, 1295 ($\nu_{\mathrm{P=O}}$), 1030, 1010, 953 ($\nu_{\mathrm{P-OPh}}$). Anal. Calcd. For C$_{18}$H$_{15}$PO$_4$: C, 66.26; H, 4.63. Found: C, 66.41; H, 4.78.

*Phenyl diphenylphosphinate (**f**)* Yield: 76%. mp: 139–143 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 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*). ^{31}P NMR (162 MHz, CDCl$_3$, δ, ppm): 30.02. IR (KBr, cm^{-1}): 3095, 3053, 3028, 1440 ($\nu_{\mathrm{P-Ph}}$), 1223 ($\nu_{\mathrm{P=O}}$), 1027, 998 ($\nu_{\mathrm{P-OPh}}$). Anal. Calcd. For C$_{18}$H$_{15}$PO$_2$: C, 73.46; H, 5.14. Found: C, 72.32; H, 5.05.

*Diphenyl phenylphosphonate (**g**)* Yield: 85%. mp: 71–76 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 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*). ^{31}P NMR (162 MHz, CDCl$_3$, δ, ppm): 11.37. IR (KBr, cm^{-1}): 3094, 3054, 3025, 1445 ($\nu_{\mathrm{P-OPh}}$), 1264 ($\nu_{\mathrm{P=O}}$), 1024, 1008, 969 ($\nu_{\mathrm{P-OPh}}$). Anal. Calcd. For C$_{18}$H$_{15}$PO$_3$: C, 69.68; H, 4.87. Found: C, 69.64; H, 4.52.

*Tri(2-iso-propylphenyl)phosphate (**h**)* Yield: 69%. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 7.35–7.15 (m, 12H, Ph-*H*), 2.88 (hept, 3H, $J = 4.00$ Hz, –C*H*(CH$_3$)$_2$), 1.12 (d, 18H, $J = 4.00$ Hz, –CH(CH_3)$_2$). ^{31}P NMR (162 MHz, CDCl$_3$, δ, ppm): −17.97. IR (KBr, cm^{-1}): 3074, 3045, 1300 ($\nu_{\mathrm{P=O}}$), 1026, 1010, 956 ($\nu_{\mathrm{P-OPh}}$). Anal. Calcd. For C$_{27}$H$_{33}$PO$_4$: C, 71.66; H, 7.35. Found: C, 71.81; H, 7.22.



	d	h	i*	j	k	l	m
R$_1$	H	CH(CH$_3$)$_2$	1-Naphthyl	Ph	H	H	F
R$_2$	H	H	H	H	Cl	F	F

* Tri(1-naphthyl)phosphate

Scheme 1. Synthesis of triphenylphosphate derivatives.

Table 1
Effects of substituted triphenyl phosphates on butadiene polymerization initiated by Fe(2-EHA)$_3$/Al^{i}Bu$_3$/donor catalyst system.[a]

Entry	Donor	Conv (%)	Microstructure [b] (%)		*rrrr* (%)	M_n [c] (10^4)	M_w/M_n [c]	T_m [d] (°C)	Xc [e] (%)
			1,2	*Cis*-1,4					
1	Triphenylphosphate (**d**)	72.3	91.5	8.5	94.5	5.8	2.5	172	69.7
2	Tri(2-isopropylphenyl)- phosphate (**h**)	61.2	94.3	5.7	94.3	6.3	2.1	177	70.2
3	Tri(2-phenylphenyl)- phosphate (**j**)	10.2	80.7	19.3	88.3	6.8	2.7	158	64.4
4	Tri(4-chlorophenyl)- phosphate (**k**)	74.9	89.7	10.3	87.8	6.0	3.0	177	65.7
5	Tri(4-fluorophenyl)- phosphate (**l**)	74.5	89.7	10.3	87.3	6.5	3.1	175	64.1
6	Tri(2,4-difluorophenyl)- phosphate (**m**)	72.7	89.0	11.0	92.9	6.3	2.7	161	67.2
7	Tri(1-naphthyl)phosphate (**i**)	55.1	91.5	8.5	94.1	12.2	3.0	179	70.1

[a] Polymerization conditions: medium, hexane; temperature, 50 °C; time, 0.5 hr for entry 4, 5 and 6, and 4 h for the others; butadiene, 0.04 mol; Fe(2-EHA)$_3$, 0.02 mmol; Al^{i}Bu$_3$, 0.6 mmol; donor, 0.08 mmol.
[b] Determined by NMR (^{1}H and ^{13}C); *rrrr*: syndiotactic index, percentage of syndiotactic pentads.
[c] GPC data in trichlorobenzene vs. polystyrene standards, n.d. denotes determined.
[d] Melting point, determined by DSC at heat rate of 10 °C/min.
[e] Estimated by the formula of $\Delta H/\Delta H_0$, ΔH was calculated by DSC and ΔH_0 referred to standard enthalpy of 1,2-PBD with 100% crystallinity, equal to 60.7 J/g.

*Tri(1-naphthyl)phosphate (**i**)* Yield: 68%. mp: 154–157 °C. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 7.95 (d, 3H, $J = 8.40$ Hz, Ph-*H*), 7.83 (d, 3H, $J = 8.00$ Hz, Ph-*H*), 7.70 (d, 3H, $J = 8.40$ Hz, Ph-*H*), 7.60 (d, 3H, $J = 7.60$ Hz, Ph-*H*), 7.50–7.46 (m, 3H, Ph-*H*), 7.42–7.37 (m, 6H, Ph-*H*). ^{31}P NMR (162 MHz, CDCl$_3$, δ, ppm): −17.15. IR (KBr, cm^{-1}): 3056, 1300 ($\nu_{P=O}$), 1041, 1013, 949 (ν_{P-OPh}). Anal. Calcd. For $C_{30}H_{21}PO_4$: C, 75.62; H, 4.44. Found: C, 75.55; H, 4.45.

*Tri(2-phenylphenyl)phosphate (**j**)* Yield: 63%. mp: 101–104 °C. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 7.26–7.14 (m, 21H, Ph-*H*), 7.09–7.05 (m, 3H, Ph-*H*), 7.00–6.99 (m, 3H, Ph-*H*). ^{31}P NMR (162 MHz, CDCl$_3$, δ, ppm): −19.51. IR (KBr, cm^{-1}): 3058, 3035, 1310 ($\nu_{P=O}$), 1049, 1012, 959 (ν_{P-OPh}). Anal. Calcd. For $C_{36}H_{27}PO_4$: C, 77.97; H, 4.91. Found: C, 78.15; H, 4.70.

*Tri(4-chlorophenyl)phosphate (**k**)* Yield: 85%. mp: 120–123 °C. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 7.33 (d, 6H, $J = 8.00$ Hz, Ph-*H*), 7.16 (d, 6H, $J = 8.00$ Hz, Ph-*H*). ^{31}P NMR (162 MHz, CDCl$_3$, δ, ppm): −18.13. IR (KBr, cm^{-1}): 3095, 3064, 1300 ($\nu_{P=O}$), 1016, 969, 958 (ν_{P-OPh}). Anal. Calcd. For $C_{18}H_{12}Cl_3PO_4$: C, 50.32; H, 2.82. Found: C, 50.40; H, 2.79.

*Tri(4-fluorophenyl)phosphate (**l**)* Yield: 72%. mp: 84–88 °C. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 7.21–7.17 (m, 6H, Ph-*H*), 7.07–7.02 (m, 6H, Ph-*H*). ^{31}P NMR (162 MHz, CDCl$_3$, δ, ppm): −17.27. IR (KBr, cm^{-1}): 3119, 3077, 3056, 1307 ($\nu_{P=O}$), 970 (ν_{P-OPh}). Anal. Calcd. For $C_{18}H_{12}F_3PO_4$: C, 56.85; H, 3.18. Found: C, 56.89; H, 3.02.

*Tri(2,4-difluorophenyl)phosphate (**m**)* Yield: 51%. mp: 57–61 °C. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 7.41–7.36 (m, 3H, Ph-*H*), 6.97–6.92 (m, 3H, Ph-*H*), 6.90–6.86 (m, 3H, Ph-*H*). ^{31}P NMR (162 MHz, CDCl$_3$, δ, ppm): −16.60. IR (KBr, cm^{-1}): 3090, 3083, 1318 ($\nu_{P=O}$), 985, 956 (ν_{P-OPh}). Anal. Calcd. For $C_{18}H_9F_6PO_4$: C, 49.79; H, 2.09. Found: C, 49.66; H, 2.14.

2.3. Procedure for butadiene polymerization

A typical procedure for the polymerization is as follows (entry 1 in Table 1): a hexane solution of butadiene (20 mL, 2.0 mol/L) was added to a moisture-free ampere capped with a rubber. Catalyst components were consecutively injected into the ampoule in the sequence of Fe(2-EHA)$_3$ (0.2 mL, 0.1 mol/L), TPP (0.16 mL, 0.5 mol/L) and Al^{i}Bu$_3$ (0.6 mL, 1.0 mol/L) to initiate polymerization. The polymerization was maintained at 50 °C for 4 h. Methanol containing 2,6-di-*tert*-butyl-4- methylphenol (1.0 wt%) was added to quench the polymerization. The mixture was poured into a large quantity of methanol to precipitate the white solid. Filtered and dried under

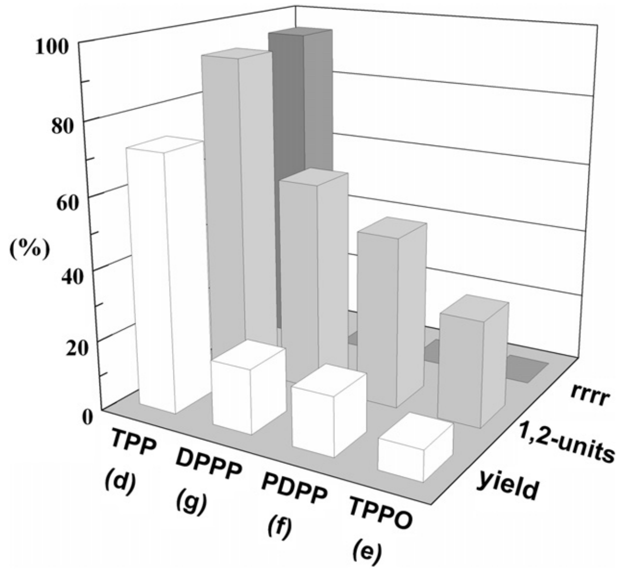


Fig. 1. The correlation between donors and catalytic performance Polymerization conditions: medium, hexane; temperature, 50 °C; butadiene, 0.04 mol; time, 4 h; Fe(2-EHA)$_3$, 0.02 mmol; Al^{i}Bu$_3$, 0.6 mmol; donor, 0.08 mmol.

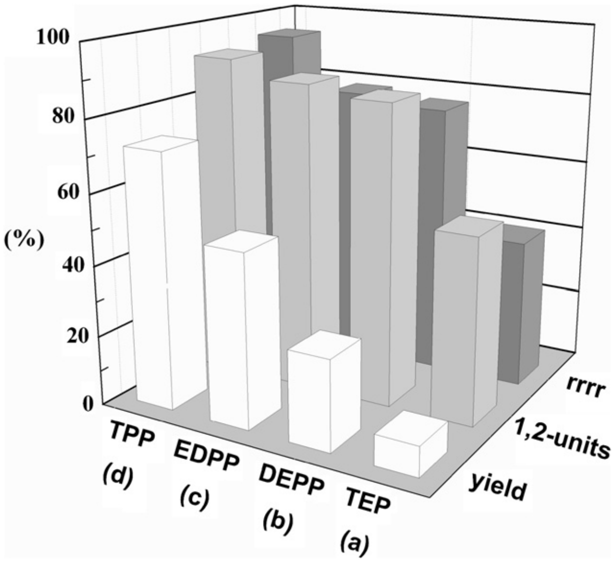


Fig. 2. Dependence of catalytic performance on structures of phosphates Polymerization conditions: medium, hexane; temperature, 50 °C; butadiene, 0.04 mol; time, 4 h (8 h for the catalyst with **e** as donor); Fe(2-EHA)$_3$, 0.02 mmol; Al^{i}Bu$_3$, 0.6 mmol; donor, 0.08 mmol.

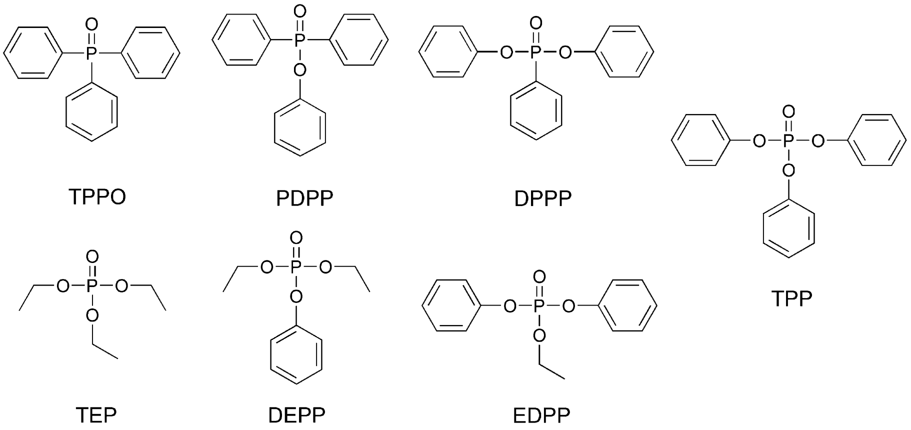


Fig. 3. The structures of seven donors.

vacuum at 40 °C for 24 h, polybutadiene was resulted at a constant weight (1.56 g, 72.3%).

2.4. Instruments and characterization methods

^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{31}P NMR (162 MHz) were recorded on a Varian Unity spectrometer in $CDCl_3$ at room temperature for P═O contained compounds or in *o*-$C_6D_4Cl_2$ at 125 °C for polymers. IR spectra were performed on BRUKE Vertex-70 FIR spectrophotometer. Elemental analyses were recorded on an elemental Vario EL spectrometer. DSC measurements were performed on a Perkin-Elmer Diamond differential scanning calorimeter at a heating rate of 10 °C/min. The number-average molecular weight (M_n) and the polydispersity index of polymer samples (M_w/M_n) were determined at 125 °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 literatures [12].

3. Results and discussions

3.1. Effects of donor

Fe(2-EHA)$_3$ had been tested as initiator for the polymerization of butadiene with the activation of aluminum alkyls or aluminum alkyl chloride (AlR_3, Al^iBu_2Cl, $AlEt_2H$ or Al^iBu_2H, R = Me, Et, ^{i}Bu, Oct) or donors (**a**–**m**). All these components alone are inactive to the polymerization of butadiene, which under the activation of aluminum alkyls or aluminum alkyl chloride, respectively, are still inert. Upon addition of the third component donor, active species are generated, which show versatile activities and 1,2 selectivities depending on the types of donors and aluminum alkyls, polymerization temperature and medium. By changing the sequence of components feeding, we find that the active species are optimally generated in the order of Fe(2-EHA)$_3$, donor and Al^iBu_3, indicating the active species could be better stabilized in the presence of such kind of donors. We carry out butadiene polymerization under the conditions ([Bd]/[Fe] = 2000, [Al]/[Fe] = 30, [P]/[Fe] = 4, temperature = 50 °C). The polymerization results are compiled in Figs. 1 and 2 and Table 1, the correlation between the structure of donors and catalytic performance can be discussed as follows.

The catalytic activity and selectivity are found to be strongly donor dependent. Phosphates (TEP, DEPP, EDPP and TPP derivatives, in Fig. 3) donated catalysts show conversion in the range of 8.5–74.9%, affording polybutadiene with mainly 1,2-structure content in the range of 56.2–94.3% and syndiotactic configuration spanning from 46.1 to 94.5% which are calculated in pentad *rrrr* by ^{13}C NMR. The melting points of polymer are varied from 147 to 179 °C. Nevertheless, as seen from Fig. 1, with TPPO, PDPP or DPPP as donor, the corresponding catalysts display remarkably low activity and poor 1,2-selectivity.

With intent to elucidate correlation between the structure of donors and catalyst performance, four compounds with structural similarity: TPPO, PDPP, DPPP and TPP (Fig. 3) are grouped and compared. Unambiguous trend of catalytic performance can be established. Replacing phenyl with phenoxyl group attached to P atom one by one, e. g. TPPO, PDPP and DPPP, increases catalytic activity and 1,2-structure content in resultant polymer. Employment of TPP, where all phenyl groups are substituted with phenoxyl group, remarkable jump in activity, 1,2-structure content (Fig. 4, polybutadiene from entry 1 in Table 1) and syndiotacticity (Fig. 5, polybutadiene from entry 1 in Table 1) of resultant polybutadiene are observed. It seems that the phenoxyl groups linked to P atom endow the catalyst with much better performance in terms of activity and 1,2-syndiotacticity.

Another four phosphates, TEP, DEPP, EDPP and TPP (Fig. 3) having ester links are also gathered, for differentiating the effects of phenoxyl and ethoxyl of donors on polymerization behaviors. Contrast to those produced from the former group donated

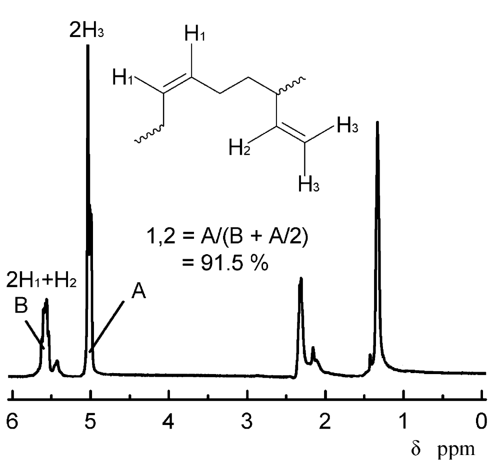


Fig. 4. The ^{1}H NMR of the obtained polybutadiene (entry 1 in Table 1, the peak of solvent around 7.26 ppm is omitted)

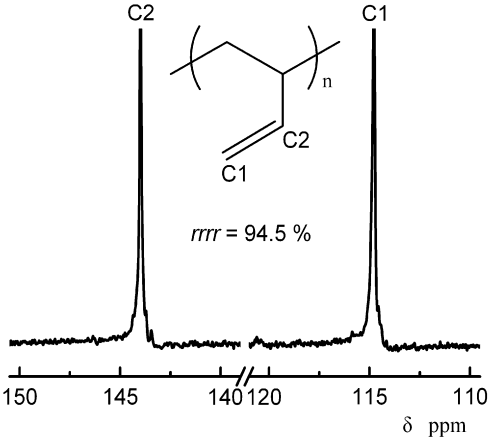
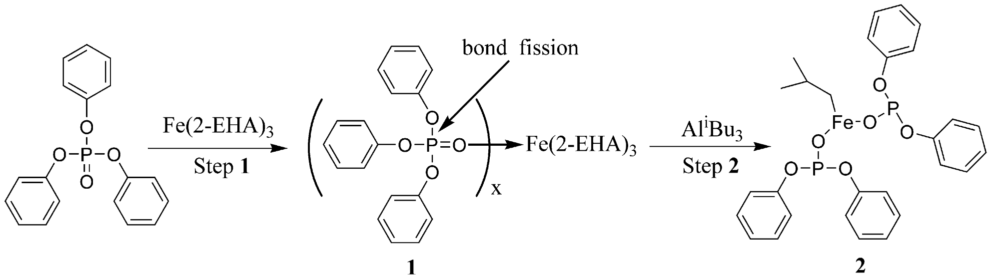


Fig. 5. The ^{13}C NMR (the olefinic region) of the obtained polybutadiene. (entry 1 in Table 1)

catalysts, the polybutadienes obtained from these donors donated catalysts are mainly 1,2-structure with high syndiotactic stereoregularity, while the activity is also strongly related to the donor used. As illustrated in Fig. 2, with TEP as donor, the formed catalyst does not lead to formation of polymer in 4 h, possibly due to the stagnant generation of active species, while polymer bearing 1,2-structure about 56.2% and syndiotactic index about 46.1% at very low activity (8.5%) is observed when polymerization is prolonged to 8 h. Presumably, the much slower generation of active not only affects the activity, but the regio- and stereoselectivity. Substituting one ethoxyl with one phenoxyl group in TEP, leads to the significantly increment of catalytic activity and improvement of polymer microstructures, and the obtained polybutadiene has mainly 1,2-structure and syndiotactic configuration. Further replacement brings about more beneficial influence on both activity and polymer microstructure. With TPP as donor, the formed catalyst is again the most excellent in this group, in terms of activity, 1,2-selectivity and stereoregularity. Concluding from the aforementioned polymerization results, phosphate donors (P atom connected with ethoxyl or phenoxyl groups) are superior to those linked with phenyl group with respect to catalytic activity, 1,2-structure selectivity and stereospecificity. Among the phosphates, donor bearing phenoxyl groups shows better catalytic performance than those with ethoxyl.

It seems that the three esters linked to P atom in donor structure are decisive for syndiospecific polymerization of butadiene in this iron catalyst system. A possible mechanism for generation of active species is proposed to rationalize the donor-dependent catalytic behaviors. Taking TPP as donor for example, as shown in Scheme 2, mixing TPP with Fe(EHA-2)$_3$ forms P=O → Fe contained complex, structurally similar to other transition metal complexes [13]. Activated by Al^{i}Bu$_3$, one bond PhO–P in complex is presumably cleaved, as –OPh of phosphate structure is widely considered as a leaving group [14], next, the iron center is alkylated to form the ^{i}Bu–Fe(OP(OPh)$_2$)$_2$ involved active species, analogous to the reported intermediate [15], though the exact structure is still unclear. The species is relatively stable in the catalytic system, due to the electron density in metal center could be largely decentralized by electron withdrawing interaction exerted by phenoxyl(s), but less efficient in the case of ethoxyl. It could be expected, depending on the structure of donors (TEP, DEPP, EDPP and TPP), the stability of the active species derived from these donors (TEP and DEPP produce the same species) increases in the sequence, ^{i}Bu–Fe(O-P(OEt)$_2$)$_2$ < ^{i}Bu–Fe(OP(OPh)(OEt))$_2$ < ^{i}Bu–Fe(OP(OPh)$_2$)$_2$, consistent with the increased order of observed catalytic performance. In the case of DPPP, PDPP or TPPO, probably the bond PhO–P is unlikely to fissile or the corresponding intermediate is less stable under the comparable conditions, thus, poor performance is observed.

With the intention of investigating effects of substituents in phenyl rings as well as accessing more effective donors on the basis of the above encouraging results for TPP, the phenyl rings of TPP are modified by electron withdrawing and bulky groups, respectively (Scheme 1). Within expectation from the aforementioned mechanism on active species formation, introduction of electron withdrawing group, chlorine or fluorine atom, to the three phenyl rings of TPP makes the cleavage of ArO–P more easily, as ArO$^-$ bearing halogen atoms is considered as a facile leaving group. The retained ArO$^-$ groups at active species can also make it more stable and more positive, due to the decentralized electronic density around the low valent (rich electronic) active species resulting from electronic withdrawing effect. Therefore, a significant jump in activity could be noticed, the yield reaching up to 72.7%–74.9% just in 0.5 h with comparison to 72.3% in 4 h in the case of TPP, irrespective of kind and position of halogen atoms (entries 4–6 in Table 1). However, both the 1,2-structure and syndiotacticity index of polymers are appreciably sacrificed, presumably, extremely fast chain propagation goes against alternately arrangement of vinyl groups on the opposite side during the polymerization. When the proton at 2-position is replaced by *iso*-propyl group, 1,2-structure is improved marginally, up to 94.3%, records the highest 1,2-selectivity in iron-based catalysts as far as we know, but the activity is somewhat decreased. It seems that the appropriate bulkiness around the center metal is favorable for 1,2 regioselectivity, while detrimental to activity due to the unfavorable bulkiness for cleavage of P–OAr linkage and monomer insertion. As expected, a drop in activity is also observed when more bulky analogue (**j**) or tri(1-naphtayl)phosphate (**i**) is used. The 1,2-selectivity of the former system slightly decrease, while the latter maintains the same selectivity as that of benchmark **d** donated catalyst.



Scheme 2. The proposed generation of active species.

Table 2
Effects of polymerization conditions on catalytic behaviors by using tri(2,4-difluorophenyl)phosphate (**m**) donated iron catalyst.

Entry	Polymerization conditions [a]			Conv (%)	Microstructure [b]		*rrrr* (%)	M_n [c] (10^4)	M_w/M_n [c]	T_m [d] (°C)	Xc [e] (%)
	Al	Temp (°C)	Time (min)		1,2 (%)	*Cis*-1,4%					
8	$Al^{i}Bu_3$	0	3 d	13.3	71.5	26.5	61.5	2.2	4.0	155	55.2
9	$Al^{i}Bu_3$	20	1 d	22.1	82.3	17.7	73.2	3.7	3.4	161	59.4
10	$Al^{i}Bu_3$	35	4 h	58.2	84.5	15.5	85.4	5.7	2.8	171	55.3
11	$Al^{i}Bu_3$	80	8	78.4	88.9	11.1	88.7	6.8	2.2	168	59.9
12	$AlMe_3$	50	30	20.4	51.5	38.2	0	n.d.	n.d.	–	–
13	$AlEt_3$	50	30	68.8	88.3	11.7	84	4.2	3.5	169	62.1
14	$AlEt_2H$	50	30	17.6	68.5	29.7	0	n.d.	n.d.	–	–
15	$Al^{i}Bu_2H$	50	30	38.7	66.0	32.9	0	n.d.	n.d.	–	–
16	$Al^{i}Bu_2Cl$	50	30	0	–	–	–	–	–	–	–
17	$Al(Oct)_3$	50	30	17.6	26.9	55.1	0	n.d.	n.d.	–	–
18	$Al^{i}Bu_3$	50	30	81.4	90.9	9.1	n.d.	n.d.	n.d.	173	64.1
19	$Al^{i}Bu_3$	50	30	58.4	78.8	19.2	n.d.	n.d.	n.d.	156	53.9
20	$Al^{i}Bu_3$	50	30	11.9	69.1	12.9	n.d.	n.d.	n.d.	153	51.4

[a] Polymerization conditions: 1,3-butadiene, 0.04 mol; $Fe(2\text{-}EHA)_3$, 0.02 mmol; Al, 0.6 mmol; donor, 0.08 mmol; solvents of entries 18, 19 and 20 are cyclohexane, toluene and dichlorobenzene, respectively.

[b] Determined by NMR (^1H and ^{13}C) and IR, the remaining is *trans*-1,4 units.

[c] GPC data in trichlorobenzene vs. polystyrene standards, n.d. denotes not determined.

[d] Melting point, determined by DSC at heat rate of 10 °C/min.

[e] Estimated by the formula of $\Delta H/\Delta H_0$, ΔH, calculated by DSC and ΔH_0 referred to standard enthalpy of 1,2-PBD with 100% crystallinity, equal to 60.7 J/g.

3.2. *Effect of polymerization conditions*

Since the activity of tri(2,4-difluorophenyl)phosphate donated catalyst system is very high, we typically investigate its catalytic performance under - various reaction conditions by changing the reaction temperature, type of activators and polymerization medium. The polymerization results are compiled in Table 2. As reflected from the data, some distinguishing polymerization features relating to the iron catalysts are observed.

Elevating the reaction temperature from 0 °C to 80 °C significantly speeds up the catalytic reactions and remarkably improves the regio- and stereospecificity (entries 6 in Table 1 and entries 8–11 in Table 2) in the current system. The yield of polymer reaches a conversion of 78.4% at 80 °C just in 8 min, while only 13.3% is obtained at 0 °C even if the polymerization time is prolonged to 72 h. More importantly, the 1,2-selectivity and pentads *rrrr*, are both increased remarkably, both reach the peak values at 50 °C, followed by an appreciably decrease at 80 °C, probably again due to the extremely fast monomer insertion and chain propagation reactions rendering polymer chain irregular. Meanwhile, the molecular weight increases, and the molecular weight distribution becomes sharper. The excellent stability of active species derived from the current catalyst system to high temperature has rarely been observed in transition metal based catalysts, never in iron based catalyst, but in some rare earth based catalysts [1b,1c,16].

In addition to $Al^{i}Bu_3$, trimethylaluminum (TMA), triethylaluminum (TEA), trioctylaluminum (TOA), diethylaluminum hydride ($AlEt_2H$), diisobutylaluminum hydride ($Al^{i}Bu_2H$) as well as diisobutylaluminum chloride ($Al^{i}Bu_2Cl$) are also used individually as cocatalyst to see whether alkylaluminums have any influence on the polymerization. TEA promoted catalyst affords polybutadiene with slight less 1,2-percentage (88.3%) and syndiotacticity (84%) in comparison of that of $Al^{i}Bu_3$ activated catalyst, possibly due to the less bulkiness around the metal center when activated by $AlEt_3$. However, far less polymer yield and much lower 1,2-selectivity are observed in the cases of the other alkylaluminums such as TMA, TOA, $AlEt_2H$, $Al^{i}Bu_2H$ and $Al^{i}Bu_2Cl$, as shown from entries 12–17 in Table 2. In deduction, the great bulkiness and appropriate alkylation ability, which $Al^{i}Bu_3$ endows with, makes it the most promising cocatalyst for stereospecific polymerization of butadiene in the current catalyst system.

Polymerization medium effects are also examined (entry 6 in Table 1 and entries 18–20 in Table 2). Aliphatic solvent like hexane and cyclohexane, serves better than toluene and dichlorobenzene, in terms of catalytic activity and stereoselectivity. This observation may be due to the competition of the nucleophilic toluene and butadiene for a vacant coordination site at the active center. Much lower activity suffered in dichlorobenzene possibly suggests the polar polymerization medium is not favored for the catalyst productivity.

4. Conclusion

A series of compounds bearing phosphoryl (P=O) have been employed in iron based catalyst systems as new donor for butadiene polymerization. The activity and selectivity of the formed catalysts are strongly related to the groups attached to P atom, and the substituents on phenyl rings of triphenylphosphate. Phosphates donated systems serve as excellent selective catalysts, actively converting butadiene to mainly 1,2-enchained syndiotactic polybutadiene. The reaction parameters such as polymerization temperature, type of catalysts and medium also play important roles in catalytic performance. Excellent tolerance to high temperature of 80 °C is unprecedently found in the current system.

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