Yttrium-catalyzed cis-1,4-Selective Polymerization of 2-(4-Halophenyl)-1,3-butadienes and Their Copolymerization with Isoprene

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Abstract  Polymerization of 2-(4-halophenyl)-1,3-butadiene (2-XPB) and their copolymerization with isoprene using a yttrium catalyst have been examined. The β-diketiminato yttrium bis(alkyl) complex (1) activated by [Ph₅C][B(C₆F₅)₄] and AlBu₃ shows high cis-1,4-selectivity (>98%) for the polymerization of 2-XPB (2-XPB = 2-FPB, 2-ClPB and 2-BrPB) to afford halogenated plastic poly(dienes) with glass transition temperatures of 30–55 °C. Moreover, the copolymerization of 2-XPB with isoprene (IP) has also been achieved by this catalyst, and the insertion ratios of 2-XPB can be facilely tuned in a full range of 0%–100% simply by changing the 2-XPB-to-IP ratio. Quantitative hydrogenation of cis-1,4-poly(2-XPB) results in perfect alternating ethylene-halostyrene copolymers, and an alternating copolymer of 4-vinylbenzoic acid with ethylene is obtained by a consecutive reaction of ethylene-4-bromostyrene copolymer with BuLi, CO₂ and HCl.

Keywords  cis-1,4-Selective; Coordination (co)polymerization; Poly(dienes); Alternating copolymer; Post-polymerization modification

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However, the highly cis-1,4-regulated poly(dienes) containing halogen groups remain scarce. Herein, we report the highly cis-1,4-selective coordination polymerization of a series of 2-(4-halophenyl)-1,3-butadienes (2-XPB, X = F, Cl and Br) using a β-diketiminato yttrium bis(alkyl) complex 1 (Chart 1). Upon the activation of $[\text{Ph}_3\text{C}]\text{[B(C_6F_5)_3]}$ and $\text{AlBu}_3$, the ternary system showed high cis-1,4-selectivity (>98%) and good control for 2-XPB polymerization with narrow molecular weight distribution. The copolymerization of 2-XPB with isoprene (IP) gave random copolymers of 2-XPB and IP. Moreover, all the poly(2-XPBs) can be easily transferred to perfect alternating copolymers of 4-halo styrene and ethylene.

**EXPERIMENTAL**

**General Considerations**

All manipulations were performed under a dry and oxygen-free nitrogen atmosphere using standard high-vacuum Schlenk techniques or in a glove box. All solvents were purified via a solvent purification system. Other reagents were purchased from Energy Chemical or Titan Chemical and used without further purification except specially mentioned. β-Diketiminato yttrium bis(alkyl) complex was prepared according to the reported literature.[26]

NMR spectra of complexes and polymers were recorded on a Bruker Avance 400 or 500 MHz spectrometer. Molecular weights and molecular weight distributions ($M_w/M_n$) of the polymers were measured by size exclusion chromatography (SEC) on a TOSOH HLC-8220 SEC instrument equipped with three Super HZM-H columns at 40 °C using THF as an eluent with a flowing rate of 0.35 mL·min$^{-1}$; the values were relative to polystyrene standards. Gel permeation chromatography (GPC) was performed with a low angle laser light scattering detector (Dawn HELOS B) to measure the molecular weights and polydispersity indexes ($M_w/M_n$) of related polymers were measured by differential scanning calorimetry (DSC) using a METTLER TOPEM DSC instrument under nitrogen flow. Any thermal history difference in the polymers was eliminated by first heating the specimen to 350 °C, cooling at 10 °C·min$^{-1}$ to room temperature, and then recording the second DSC scan from 25 °C to 350 °C at 10 °C·min$^{-1}$.

**Synthesis of 2-(4-Halophenyl)-1,3-butadiene (2-XPB)**

To a stirred solution of 4-haloacetophenone (0.1 mol) in THF (100 mL), a solution of vinylmagnesium bromide (120 mL, 1.0 mol·L$^{-1}$) was added dropwise in THF, 0.12 mol, 1.2 equiv., pre-heated to 40 °C to dissolve vinylmagnesium bromide) was added via a syringe at 0 °C under an nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 4 h and then poured into an iced 10% HCl aqueous solution (200 mL) and extracted with ethyl acetate (300 mL). The extract was concentrated via rotary evaporation, followed by adding pyridinium $p$-toluene sulfonate. The mixture was distilled at 120 °C under vacuum, with an ethanol/ice bath cooled receiving flask. The crude product was further purified through a silica column using 30–60 °C petro ether as eluent followed by rotary evaporation. Polymerization grade monomers were further dried with CaH$_2$ overnight to remove trace moisture.

**Typical Polymerization Procedure (Table 1, Entry 1)**

A 10 mL penicillin bottle equipped with a stir bar was charged with 2-FPB (0.30 g, 2 mmol), 0.1 mL of $\text{AlBu}_3$ solution in toluene (0.5 mol·L$^{-1}$) and 1 mL of toluene. The mixture was stirred until 2-FPB dissolved to obtain the monomer solution. Another 10 mL penicillin bottle was charged with 2-(4-halophenyl) imidazolyl yttrium bis(alkyl) complex (6.4 mg, 10 μmol), $[\text{Ph}_3\text{C}]\text{[B(C_6F_5)_3]}$ (9.2 mg, 10 μmol), 0.1 mL of $\text{AlBu}_3$ solution in toluene (0.5 mol·L$^{-1}$) and 0.9 mL of toluene. The mixture was stirred until the catalyst and borate dissolved to get the catalyst solution. The catalyst solution was poured into the monomer solution under stirring and the polymerization was carried out for 2 min. The polymerization was quenched with an ethanol solution acidified with 10% hydrochloric acid. The polymer was dissolved in 2 mL of CHCl$_3$ and precipitated in ethanol for 3 times. The polymer was dried to constant weight in a vacuum oven at 40 °C for 24 h (> 99% isolated yield).

**Typical Hydrogenation Procedure**

A 50 mL round-bottom flask equipped with a stir bar and a reflux condensing tube was charged with poly(2-FPB) (0.6 g, 4 mmol), $p$-tosyl hydrazide (2.2 g, 12 mmol, 3 equiv.), tri-propylamine (1.7 g, 12 mmol, 3 equiv.) and toluene (25 mL) and filled with nitrogen. The mixture was heated to 100 °C for 24 h. Toluene was removed via rotary evaporation. The resulting polymer was dissolved in 10 mL of CHCl$_3$ and precipitated in 200 mL of ethanol for 3 times to remove other byproducts. The polymer was dried to constant weight in a vacuum oven at 40 °C for 24 h.

**Synthesis of Poly(StCOOH-alt-E)**

To a 25 mL ampoule were added poly(BrSt-alt-E) (0.42 g, 2 mmol) and anhydrous THF (10 mL). The ampule was cooled in liquid N$_2$, pumped to vacuum and refilled with high-pure nitrogen for 3 times. Then the ampule was put in a ~20 °C bath. To the ampule was slowly added 1 mL of $\text{BuLi}$ (toluene solution, 2.5 mol·L$^{-1}$, 1.25 equiv.) via syringe and stirred for 20 min. White to pale yellow powder precipitated from the solution. The ampule was subsequently filled with CO$_2$, stirring for 10 min and quenched with 10% HCl aqueous solution. The polymer was purified by dissolving in NaOH aqueous solution followed by precipitating in HCl aqueous solution, affording yellow powder product. The polymer was dried to constant weight in a vacuum oven at 40 °C for 24 h.

**RESULTS AND DISCUSSION**

**Homopolymerization of 2-XPB**

A series of 2-XPB monomers were synthesized through the dehydration of 2-(4-halophenyl)but-3-en-2-ol using pyridinium $p$-toluene sulfonate (PPTS) as the dehydrating agent (Scheme 1). The polymerization of 2-FPB was carried out using a ternary system $1/\text{AlBu}_3/[\text{Ph}_3\text{C}]\text{[B(C_6F_5)_3]}$ and reached a complete conversion in 2 h with a high cis-1,4-selectivity (cis-1,4-content: 98.6%). Table 1, Entry 1), albeit much slower than isoprene polymerization under the same condition.[28] On increasing the monomer-to-Y ratio from 400/1 to 1200/1 (Table 1, entries 2–4),

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the molecular weight increased correspondingly from $3.11 \times 10^4$ g·mol$^{-1}$ to $6.95 \times 10^4$ g·mol$^{-1}$ despite lower than the theoretical molecular weight, which may be ascribed to the presence of the chain-transfer reaction to aluminum tri-alkyls. All polymers possessed narrow molecular weight distributions ($M_w/M_n \leq 2.01$), indicating a single-site catalyst behavior. Increasing the polymerization temperature resulted in a significant decrement of cis-1,4-selectivity (cis-1,4-content: 96.1% at 40 °C and 91.5% at 60 °C, Table S1, entries 2 and 3, in the electronic supplementary information, ESI). Meanwhile, higher polymerization temperature also led to a slightly reduced molecular weight and a wider molecular weight distribution, indicating an accelerated chain-transfer reaction. When the polymerizations of 2-ClPB and 2-BrPB were carried out using this catalyst, the highly cis-1,4-regulated products were also obtained in high activities (cis-1,4-content: 98.8% for poly(2-ClPB), 98.7% for poly(2-BrPB), Table 1, entries 5 and 6), which is in sharp contrast to that observed in the coordination polymerization of halogenated styrenes.

All the resulting poly(2-XPB)s were well-proved by 1H-NMR and 13C-NMR spectra. As is shown in Fig. 1, the signal at 5.4 ppm is ascribed to the internal olefinic proton H3 and the resonances for the terminal vinyl protons from 3,4-unit at ca. 4.8 and 5.1 ppm are almost absent, suggesting the high cis-1,4-regularities of these poly(2-XPB)s. In the 13C-NMR spectra, the signals at 139 and 129 ppm are assigned to C2 and C3 from the main-chain while the signals at 29.5 and 27.6 ppm represent C1 and C4, respectively (see Figs. S2−S4 in ESI). The carbons from the phenyl ring in poly(2-FPB) show double peaks

### Table 1 Homopolymerization of 2-XPB by complex 1.

| Entry | Monomer [M]/[Y] | Conv. (%) | cis-1,4-content | $M_w$ ×10$^{-4}$ | $M_w/M_n$ | $T_g$ (°C) |
|-------|----------------|-----------|-----------------|----------------|-----------|------------|
| 1     | 2-FPB 200      | >99       | 98.6            | 1.71            | 1.39      | 30.3       |
| 2     | 2-FPB 400      | >99       | 98.4            | 3.11            | 1.46      | 29.7       |
| 3     | 2-FPB 800      | >99       | 98.2            | 4.78            | 1.76      | 30.6       |
| 4     | 2-FPB 1200     | >99       | 98.2            | 6.95            | 2.01      | 31.0       |
| 5     | 2-ClPB 200     | >99       | 98.8            | 2.51            | 1.73      | 50.1       |
| 6     | 2-BrPB 200     | >99       | 98.7            | 2.52            | 1.34      | 55.0       |

*Conditions: BDI-Y 10 μmol, [Ph$_3$C][B(C$_6$F$_5$)$_4$] 10 μmol, Al$_i$Bu$_3$ 100 μmol, time 2 h, temperature 25 °C, toluene 2 mL. cis-1,4-Content, determined by 1H-NMR spectroscopy in CDCl$_3$. Determined by GPC in THF at 40 °C against polystyrene standard. Measured by DSC.*

All the resulting poly(2-XPB)s were well-proved by 1H-NMR and 13C-NMR spectra. As is shown in Fig. 1, the signal at 5.4 ppm is ascribed to the internal olefinic proton H3 and the resonances for the terminal vinyl protons from 3,4-unit at ca. 4.8 and 5.1 ppm are almost absent, suggesting the high cis-1,4-regularity of these poly(2-XPB)s. In the 13C-NMR spectra, the signals at 139 and 129 ppm are assigned to C2 and C3 from the main-chain while the signals at 29.5 and 27.6 ppm represent C1 and C4, respectively (see Figs. S2–S4 in ESI). The carbons from the phenyl ring in poly(2-FPB) show double peaks

**Scheme 1** Syntheses of 2-XPB monomers.

**Fig. 1** 1H-NMR spectra of polar poly(2-XPB)s.

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because of C-F coupling and the resultant coupling constant depends on the distance between the carbon and fluorine (1JC1F=245 Hz, 2JC1F=21.25 Hz, 3JC1F=7.5 Hz and 4JC1F=3.75 Hz). Moreover, the resulting polymers perform as plastics possessing rather high Tg (poly(2-FPB): 30.3 °C, poly(2-ClPB): 50.1 °C, poly(2-BrPB): 55.0 °C) instead of a typical rubber because of the large pendant phenyl groups that limit free rotation of the main chain.

Copolymerization of 2-XPB with Isoprene

The copolymerization of 2-FPB with isoprene was carried out in toluene at 25 °C using complex 1 and reached a high conversion in 1 h (Table 2). The comonomer content varied from 21.6% to 65.7% by changing the feed ratio. All copolymers possessed narrow molecular weight distributions. Different from the tapered copolymer of 2-MOPB with isoprene reported previously,[12] these copolymers had a single Tg rising almost linearly with the increase of 2-FPB content (Fig. 2), indicating that the copolymers had random sequences. To further explore the sequence distribution of the copolymers, kinetics of copolymerization was investigated at low conversions (<10%). The competitive reactivity ratios were detected (rIP=0.94, r2-FPB=0.14, R2=0.996, Fig. 3), confirming the random sequence distributions. Similarly, the copolymers of 2-CIPB/2-BrPB with IP also possess a single Tg linearly dependent on the comonomer content, suggesting that all copolymers possess random sequence distributions. It is noteworthy that 2-FPB did not show superiority to isoprene, which might contribute to the weak coordination ability of the fluorine substituent as well as its electron withdrawing effect that lowered the electron density of the conjugated diene compared with that in 2-MOPB (surface electrostatic potential distributions of 2-XPB monomers are given in Fig. S40 in ESI).

The NMR signal of the copolymer is closely related to its backbone structure. The resonance signals of protons connected to carbon C3 (Hc3 and Hf3) in all copolymers are integrated to calculate the comonomer content (1H-NMR spectra are shown in Figs. S5–S13 in ESI). All peaks are much broader than the corresponding homopolymers, suggesting the existence of large number of connection sites in the copolymers.

In the 13C-NMR spectrum (Fig. 4), the signals of the alkyl regions are assigned. The signals at 23.47, 18.57 and 16.05 ppm

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**Table 2** Copolymerization of 2-XPB with IP by complex 1.

| Entry | 2-XPB | [2-XPB]/[IP]/[Y] | Conv. (%) | 2-XPB content b (%) | Mw/Mn c | Tg d (°C) |
|-------|-------|-----------------|-----------|---------------------|---------|-----------|
| 1     | 2-FPB | 100/300/1       | 97.1      | 21.6                | 3.67    | 1.56      | −42.9    |
| 2     | 2-FPB | 200/200/1       | 90.7      | 46.0                | 4.32    | 1.42      | −20.7    |
| 3     | 2-FPB | 300/100/1       | 86.3      | 65.7                | 5.10    | 1.78      | 4.0      |
| 4     | 2-CIPB| 100/300/1       | 91.9      | 19.8                | 3.26    | 1.84      | −42.5    |
| 5     | 2-CIPB| 200/200/1       | 89.1      | 39.5                | 3.18    | 1.85      | −13.5    |
| 6     | 2-CIPB| 300/100/1       | 85.7      | 68.6                | 4.11    | 1.75      | 21.0     |
| 7     | 2-BrPB| 100/300/1       | 92.7      | 22.9                | 4.58    | 1.70      | −31.6    |
| 8     | 2-BrPB| 200/200/1       | 92.7      | 42.6                | 3.74    | 1.66      | −5.1     |
| 9     | 2-BrPB| 300/100/1       | 86.3      | 68.5                | 3.91    | 1.73      | 30.3     |

a Conditions: BDI·Y 10 μmol, [Ph3C][B(C6F5)4] 10 μmol, AIBN 100 μmol, time 1 h, temperature 25 °C, toluene 2 mL. b Determined by 1H-NMR spectroscopy in CDCl3. c Determined by GPC in THF at 40 °C against polystyrene standard. d Measured by DSC.

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**Fig. 2** The relationship between the glass transition temperature and the comonomer content (−66 °C for polyisoprene).
represent the methyl carbon of isoprene with cis-1,4-, 3,4- and trans-1,4-units, respectively. The $^{13}$C-NMR spectrum clearly demonstrates high cis-1,4-regularity (>98%) of the copolymer. According to the $^{13}$C-NMR spectra of poly(IP) and poly(2-FPB), all signals of poly(IP) and poly(2-FPB) segments can be assigned clearly (32.19 ppm: $\text{I} \rightarrow \text{C}_{1}$I, 29.91 ppm: $\text{F} \rightarrow \text{C} \text{I}$F, 27.65 ppm: $\text{C}_{4} \text{F} \rightarrow \text{F}$, 26.46 ppm: $\text{C}_{4} \text{I} \rightarrow \text{I}$), whilst signals at 31.90, 30.26, 27.17 and 26.94 ppm possess the same integral value, indicating the connection sites of different monomers. Thus, the signals at 31.90 and 30.26 ppm represent $\text{F} \rightarrow \text{C} \text{I}$F and $\text{I} \rightarrow \text{C} \text{I}$I, respectively. Further characterization of heteronuclear multiple bond correlation (HMBC) spectrum helps with the assignment of signals at 27.17 and 26.94 ppm. In the HMBC spectrum (Fig. 5), $\text{C}_{4}$F $\rightarrow$ I shows coupling with $\text{H}_{\text{C}2}$ (5.51, 26.82), while $\text{C}_{4}$I $\rightarrow$ F only shows coupling with $\text{H}_{\text{C}3}$ (5.00, 27.20). Thus, signals at 27.17 and 26.94 ppm represent $\text{C}_{4}$I $\rightarrow$ F and $\text{C}_{4}$F $\rightarrow$ I, respectively. Furthermore, the signal at 26.94 ppm shows similar shape to that of the signal at 27.65 ppm while the signal at 27.17 ppm shows similar shape to 26.46 ppm (Fig. S14 in ESI), which also indirectly proves the assignment. The copolymers of 2-CIPB/2-BrPB with isoprene also possess highly cis-1,4-regularities (determined by $^{13}$C-NMR for Table 2, entries 6 and 9, Figs. S15 and S16 in ESI). All these results definitely prove that such complex I based catalytic system shows good polar group tolerance in the copolymerization of 2-XPB with IP, affording random copolymers poly(2-XPB-co-IP) with high cis-1,4-regularities.

**Hydrogenation and Post-polymerization Modification**

Alternating copolymers of ethylene and styrene derivatives are usually synthesized via ethylene copolymerization with styrene derivatives using specific transition-metal catalysts[28,29]. The hydrogenation of cis-1,4-regular poly(dienes) is another convenient method.[30] Therefore, the perfect alternating copolymers of ethylene and 4-halostyrenes are quantitatively produced by the reaction of cis-1,4-poly(2-XPB) with p-tosyl hydrazide (Scheme 2), which are difficult to be generated by direct copolymerization of ethylene and 4-halostyrenes. The $^{13}$C-NMR spectra clearly indicate the perfect alternate structure of the resulting copolymers (Fig. 6). The resonance of $\text{C}_{4}$ shows a triplet, indicating that atactic copolymers are obtained[31]. All the hydrogenated products possess glass transition temperatures close to their poly(dienes) substrates (poly(FSt-alt-E): 38.9 °C, poly(CISt-alt-E): 48.5 °C, poly(BrSt-alt-E): 54.7 °C, Figs. S36–S38 in ESI).

![Scheme 2](https://doi.org/10.1007/s10118-021-2505-3)

**Fig. 5** Part of HMBC spectrum of the copolymer of 2-FPB with IP (Table 2, entry 3, CDCl$_3$, 25 °C).

**Fig. 6** $^{13}$C-NMR spectra of poly(XSt-alt-E) (CDCl$_3$, 25 °C).
CONCLUSIONS

In summary, we have demonstrated that the highly cis-1,4-selective polymerization of 2-(4-halophenyl)-1,3-butadiene (2-XPB) and their copolymerization with isoprene can be achieved using a β-diketiminato yttrium catalyst. The electron-withdrawing halogen on the aromatic ring exerts little influence on the polymerization behavior and, therefore, the random copolymers of 2-XPB and isoprene with variable 2-XPB contents were afforded. Hydrogenation of poly(2-XPB) was carried out quantitatively under mild homogeneous conditions to generate hydrogenated product by NMR analysis was performed in D_{2}O containing sodium hydroxide at 25 °C (Fig. S22 in ESI). The signal at 175 ppm assigned to the carboxylate carbon confirms the existence of carboxyl groups. Furthermore, the FTIR spectroscopy analysis demonstrates that the hydroxyl stretching band is observed at ca. 3500−2500 cm\(^{-1}\) and the carbonyl stretching band appears at 1704 cm\(^{-1}\) (Fig. S23 in ESI).

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-021-2505-3.

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