## Supporting Information

# Rare-earth Metal-Catalyzed Highly 3,4-Regioselective Polymerization of Polar 1-Phenyl-1,3-Butadiene Derivates 

Fen You, ${ }^{+}$Xiaoyu Wang, ${ }^{+}$Wenyu Shi, Xuyang Yan, and Xiaochao Shi

Department of Polymer Materials, School of Materials Science and Engineering, Shanghai
University, Materials Building, Nanchen Street 333, Shanghai 200444, China.


Figure S1. ${ }^{1} \mathrm{H}$ NMR spectrum of monomer $\boldsymbol{p}$-FPB. $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25{ }^{\circ} \mathrm{C}\right)$


Figure S2. ${ }^{13} \mathrm{C}$ NMR spectrum of monomer $\boldsymbol{p}$-FPB. $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25{ }^{\circ} \mathrm{C}\right)$


Figure S3. ${ }^{1} \mathrm{H}$ NMR spectrum of monomer $\boldsymbol{o}$-FPB. $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25{ }^{\circ} \mathrm{C}\right)$



Figure S4. ${ }^{13} \mathrm{C}$ NMR spectrum of monomer $\boldsymbol{o}$-FPB. ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25{ }^{\circ} \mathrm{C}$ )


Figure $\mathrm{S} 5 .{ }^{1} \mathrm{H}$ NMR spectrum of monomer $\boldsymbol{m}$-FPB. $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25{ }^{\circ} \mathrm{C}\right)$



Figure S6. ${ }^{13} \mathrm{C}$ NMR spectrum of monomer $\boldsymbol{m}$-FPB. $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25{ }^{\circ} \mathrm{C}\right.$ )


Figure S7. ${ }^{1} \mathrm{H}$ NMR spectrum of monomer $\boldsymbol{p}$-CIPB. $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}\right)$


Figure S8. ${ }^{13} \mathrm{C}$ NMR spectrum of monomer $\boldsymbol{p}$-CIPB. ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25{ }^{\circ} \mathrm{C}$ )


Figure $\mathrm{S} 9 .{ }^{1} \mathrm{H}$ NMR spectrum of monomer $\boldsymbol{p}$-BrPB. $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25{ }^{\circ} \mathrm{C}\right)$


Figure $\mathrm{S} 10 .{ }^{13} \mathrm{C}$ NMR spectrum of monomer $\boldsymbol{p}$-BrPB. ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}$ )


Figure $\mathrm{S} 11 .{ }^{1} \mathrm{H}$ NMR spectrum of monomer $\boldsymbol{p}$-NPB. $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25{ }^{\circ} \mathrm{C}\right.$ )


Figure S12. ${ }^{13} \mathrm{C}$ NMR spectrum of monomer $\boldsymbol{p}$-NPB. ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}$ )


Figure S13. ${ }^{1} \mathrm{H}$ NMR spectrum of monomer $\boldsymbol{p}$-SPB. $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}\right.$ )


Figure S14. ${ }^{13} \mathrm{C}$ NMR spectrum of monomer $\boldsymbol{p}$-SPB. ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25{ }^{\circ} \mathrm{C}$ )


Figure S15．${ }^{1} \mathrm{H}$ NMR spectrum of monomer $\boldsymbol{p}$－OPB．（ $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25{ }^{\circ} \mathrm{C}$ ）


Figure $\mathrm{S} 16 .{ }^{13} \mathrm{C}$ NMR spectrum of monomer $\boldsymbol{p}$－OPB．（ $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}$ ）


Figure S17. ${ }^{1} \mathrm{H}$ NMR spectrum of poly $(\boldsymbol{p}-\mathbf{F P B})$ prepared by complex 4. (Entry 5, Table 1)


Figure S18. ${ }^{1} \mathrm{H}$ NMR spectrum of poly $(\mathbf{1 P B})$ prepared by complex 1. (Entry 1, Table 2)


Figure S19. ${ }^{13} \mathrm{C}$ NMR spectrum of poly $(\mathbf{1 P B})$ prepared by complex 1. (Entry 1, Table 2)


Figure $\mathrm{S} 20{ }^{1} \mathrm{H}$ NMR spectrum of poly $(\boldsymbol{m}-\mathbf{F P B})$ prepared by complex 1. (Entry 2, Table 2)


Figure S21. ${ }^{13} \mathrm{C}$ NMR spectrum of $\operatorname{poly}(\boldsymbol{m}-\mathbf{F P B})$ prepared by complex 1. (Entry 2, Table 2)


Figure S22. ${ }^{1} \mathrm{H}$ NMR spectrum of poly( $\left.\boldsymbol{o}-\mathbf{F P B}\right)$ prepared by complex 1 . (Entry 3, Table 2)


Figure S23. ${ }^{1} \mathrm{H}$ NMR spectrum of poly( $\boldsymbol{p}-\mathbf{C I P B}$ ) prepared by complex 1. (Entry 4, Table 2)


Figure S24. ${ }^{1} \mathrm{H}$ NMR spectrum of poly( $\boldsymbol{p}$-SPB) prepared by complex 1. (Entry 4, Table 2)


Figure S25. ${ }^{1} \mathrm{H}$ NMR spectrum of $\operatorname{poly}(\boldsymbol{p}-\mathbf{O P B})$ prepared by complex 1. (Entry 4, Table 2)

Scheme S1. Homopolymerization of 1-(4-fluorophenyl)-1,3-butadiene (p-FPB) with bis(phosphinophenyl)amido yttrium complex. ${ }^{a}$


Yield: $65.5 \%(3 \mathrm{~h}) ; \quad M_{\mathrm{n}}=1.68 \times 10^{4}, M_{\mathrm{w}} / M_{\mathrm{n}}=1.25 ; 3,4$-regularity: $>99 \%$


Figure S26. ${ }^{13} \mathrm{C}$ NMR spectra of copolymer prepared by complex 1. (Entry 1, Table 3)


Figure S27. ${ }^{13} \mathrm{C}$ NMR spectra of copolymer prepared by complex 1. (Entry 2, Table 3)


Figure S28. ${ }^{13} \mathrm{C}$ NMR spectra of copolymer prepared by complex 1. (Entry 3, Table 3)


Figure S29. ${ }^{13} \mathrm{C}$ NMR spectra of copolymer prepared by complex 1. (Entry 4, Table 3)


Figure S30. ${ }^{13} \mathrm{C}$ NMR spectra of copolymer prepared by complex 1. (Entry 5, Table 3)


Figure S 31 . GPC curves of $\operatorname{poly}(\boldsymbol{p} \mathbf{- F P B})$ prepared by complex 1. (From left to right: Entry 2, Table 1; Entry 8, Table 1; Entry 9, Table 1).


Figure S32. GPC curves of polymers with substitutents at the para position of the phenyl ring prepared by complex 1. (From left to right: Entry 2, Table 2; Entry 3, Table 2; c: Entry 4, Table 2).


Figure S33 GPC curves of copolymers prepared by complex 1. (Entries in Table 3).


Figure S34. DSC curves of copolymers prepared by complex 1. (Entries in Table 3).


Figure S35. TGA curve of a poly(1PB) prepared by complex 1. (Entry 1, Table 2).


Figure S36. TGA curve of a poly( $\boldsymbol{p}-\mathbf{F P B}$ ) prepared by complex 1. (Entry 7, Table 1).


Figure S37. TGA curve of a poly( $\boldsymbol{m}-\mathbf{F P B})$ prepared by complex 1. (Entry 2, Table 2).


Figure S38. TGA curve of a poly(o-FPB) prepared by complex 1. (Entry 3, Table 2).


Figure S39. TGA curve of a poly( $\boldsymbol{p}-\mathbf{C I P B})$ prepared by complex 1. (Entry 4,Table 2).


Figure S40. TGA curve of a poly( $\boldsymbol{p}-\mathbf{N P B}$ ) prepared by complex 1. (Entry 6,Table 2).


Figure S41. TGA curve of a poly( $\boldsymbol{p}-\mathbf{O P B}$ ) prepared by complex 1. (Entry 7,Table 2).


Figure S42. TGA curve of a poly( $\boldsymbol{p}-\mathbf{S P B}$ ) prepared by complex 1. (Entry 8,Table 2).

