Table S1 the effect of Li/B to polymer properties

Li/B	conversion	M_n (g·mol^{-1})	M_w/M_n	hydroxyl value (mmol·g^{-1})	*cis*-1,4
5:2	36%	91831	1.6	0.0207	85%
1:2	94%	87392	1.3	0.0224	96%
1:3	95%	64633	1.5	0.0282	95%
1:4	98%	58678	1.9	0.0273	96%
1:8	97%	37696	2.3	0.0364	97%

polymerization condition：Nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=10:1, 50℃, 4h.

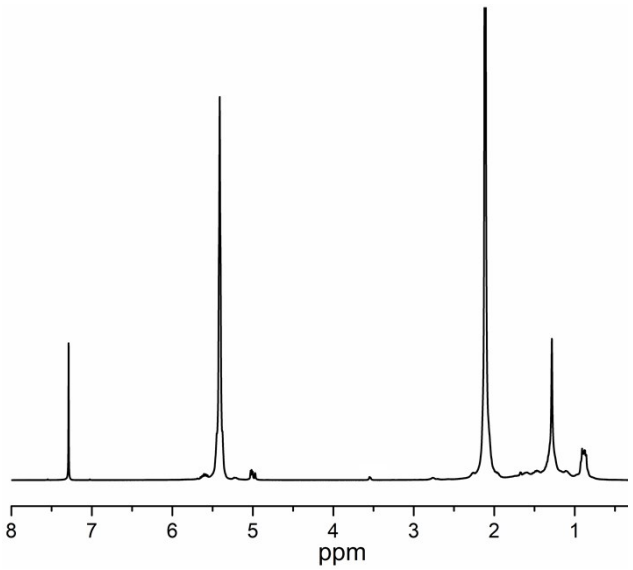

Figure S1 the ^{1}H NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=10:1, Li/B=5:2, 50℃, 4h)

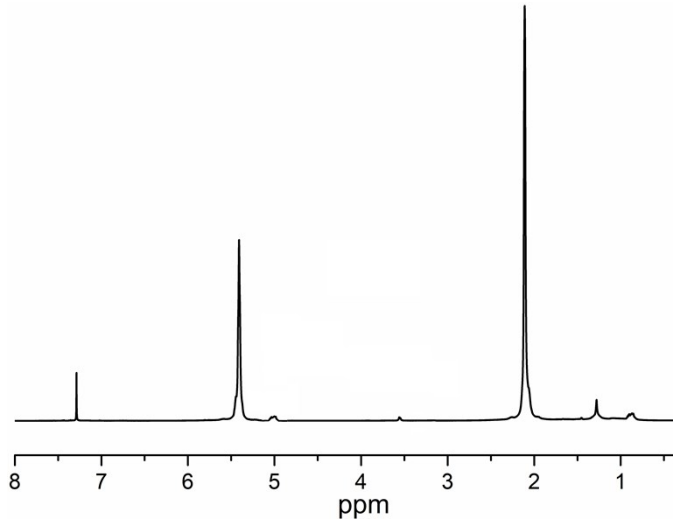

Figure S2 the ^{1}H NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=10:1, Li/B=1:2, 50℃, 4h)

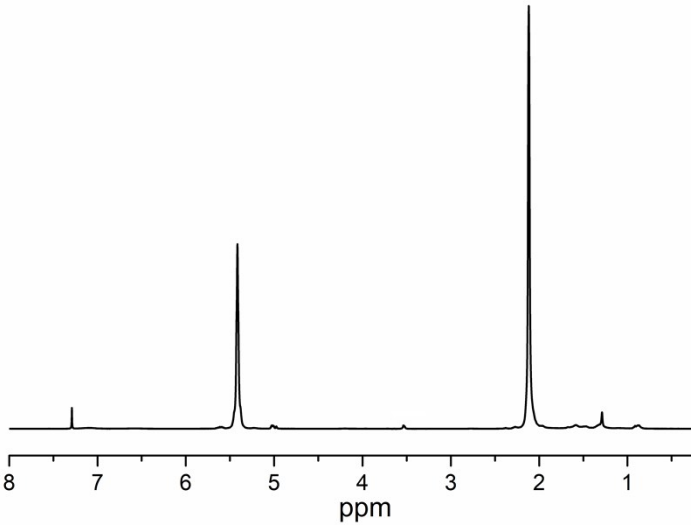

Figure S3 the ^{1}H NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=10:1, Li/B=1:3, 50℃, 4h)

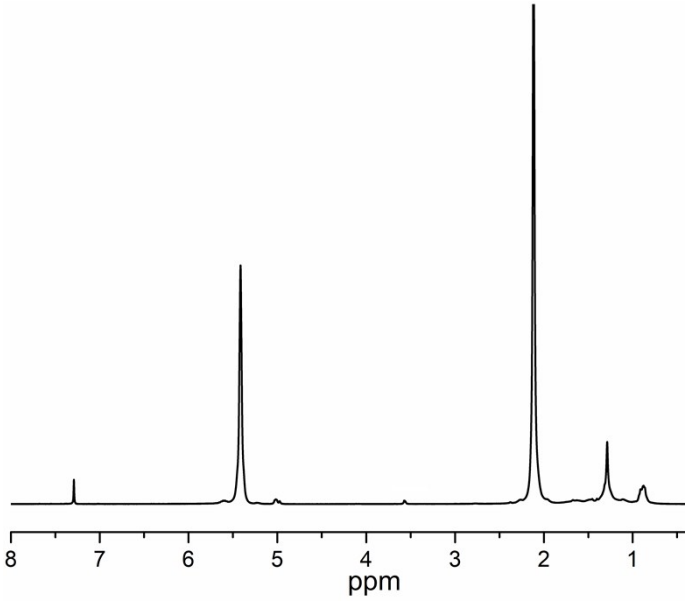

Figure S4 the ^{1}H NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=10:1, Li/B=1:4, 50℃, 4h)

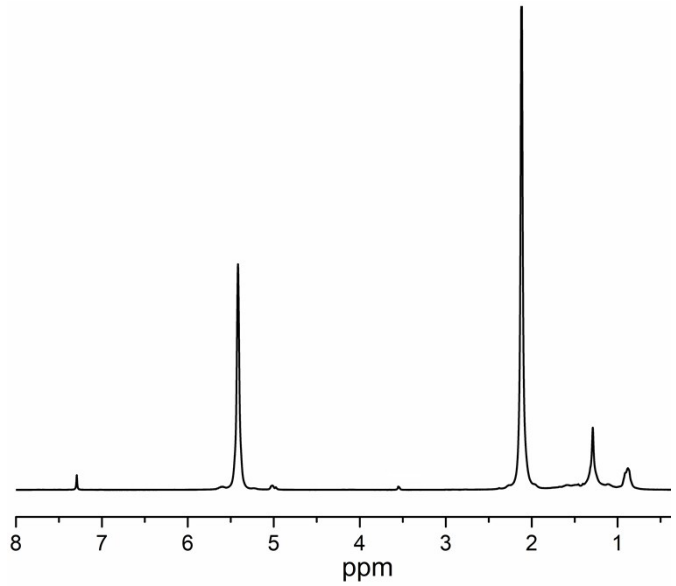

Figure S5 the ^{1}H NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=10:1, Li/B=1:8, 50℃, 4h)

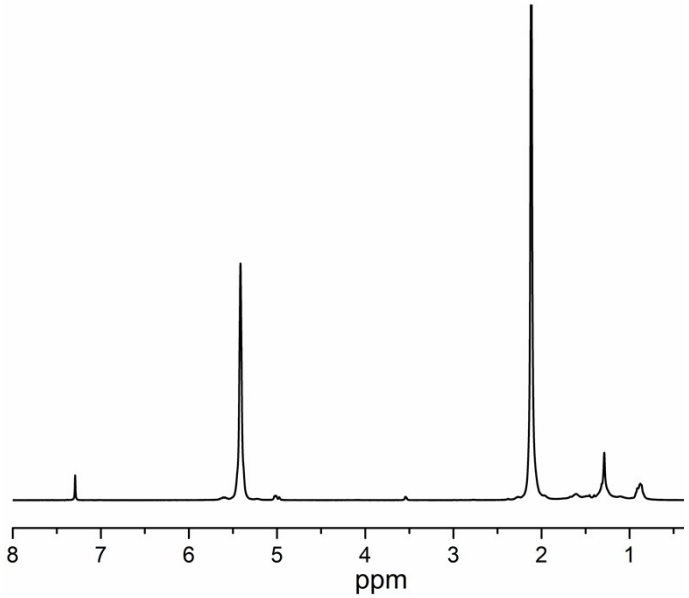

Figure S6 the ^{1}H NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=2.5:1, Li/B=1:2, 50℃, 4h)

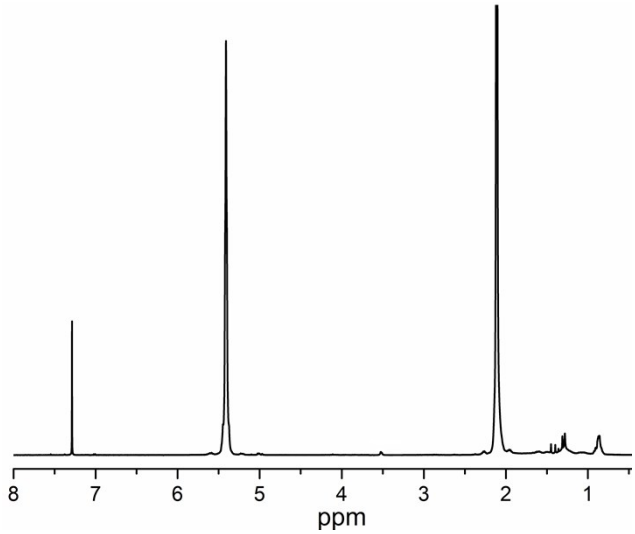

Figure S7 the ^{1}H NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=5:1, Li/B=1:2, 50℃, 4h)

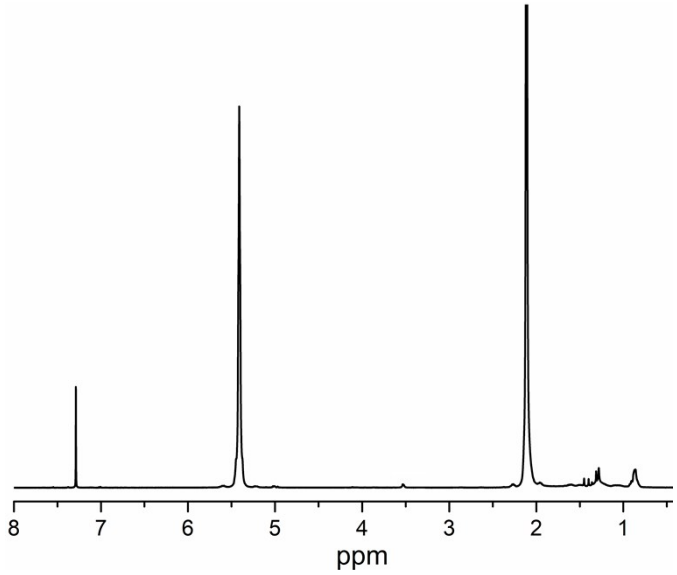

Figure S8 the ^{1}H NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=10:1, Li/B=1:2, 50℃, 4h)

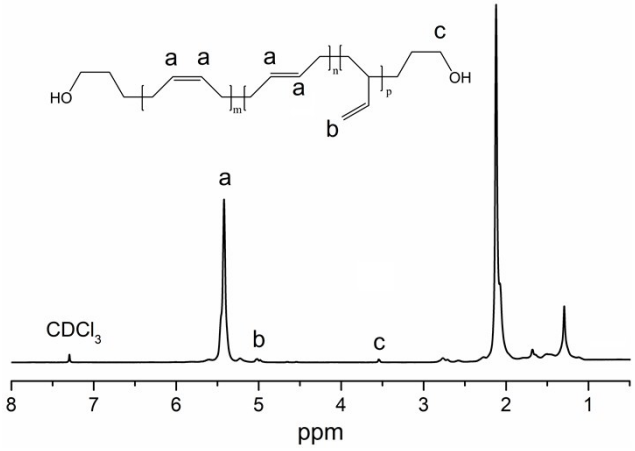

Figure S9 the ^{1}H NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=20:1, Li/B=1:2, 50℃, 4h)

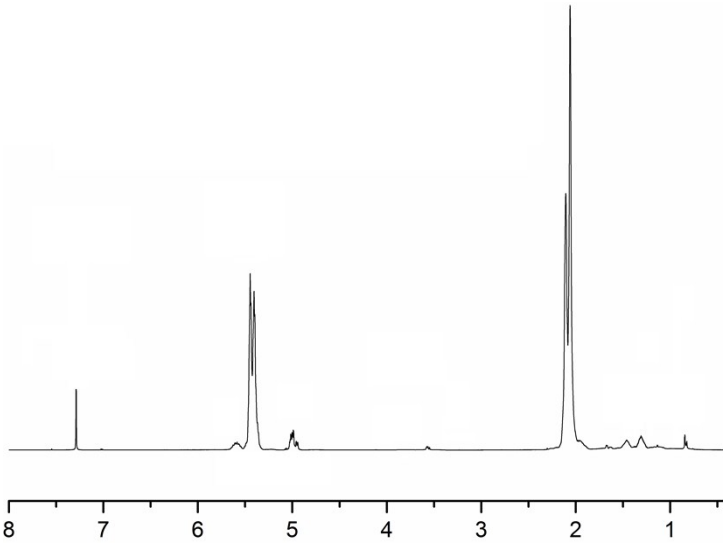

Figure S10 the ^{1}H NMR spectrum of HTPB (polymerization process: Li amount: 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml, 50℃, 4h.)

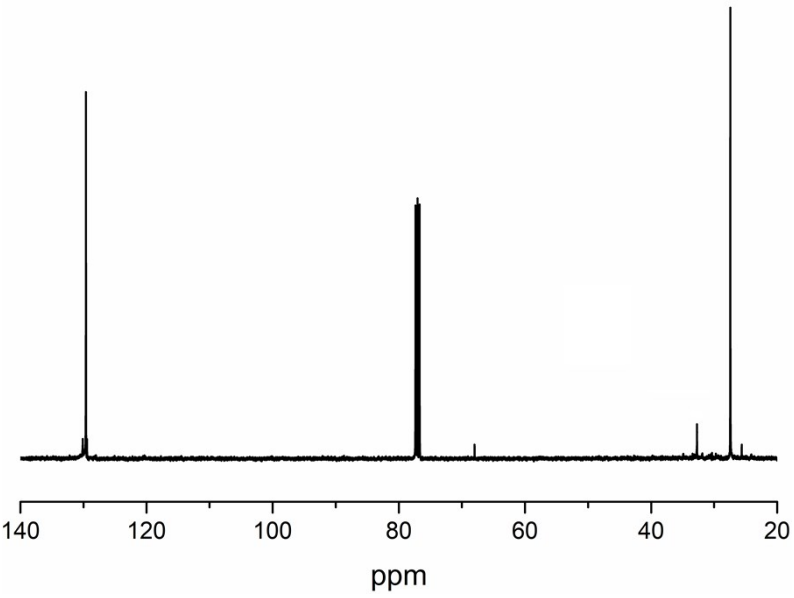

Figure S11 the ^{13}C NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=10:1, Li/B=5:2, 50℃, 4h)

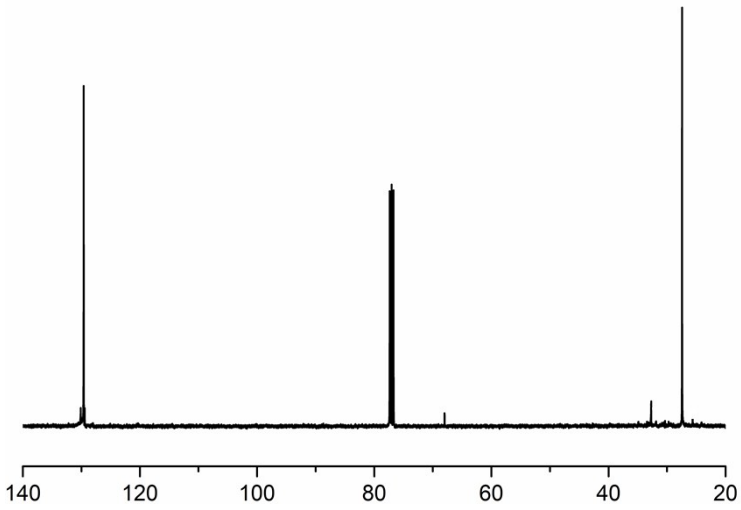

Figure S12 the ^{13}C NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=10:1, Li/B=1:2, 50℃, 4h)

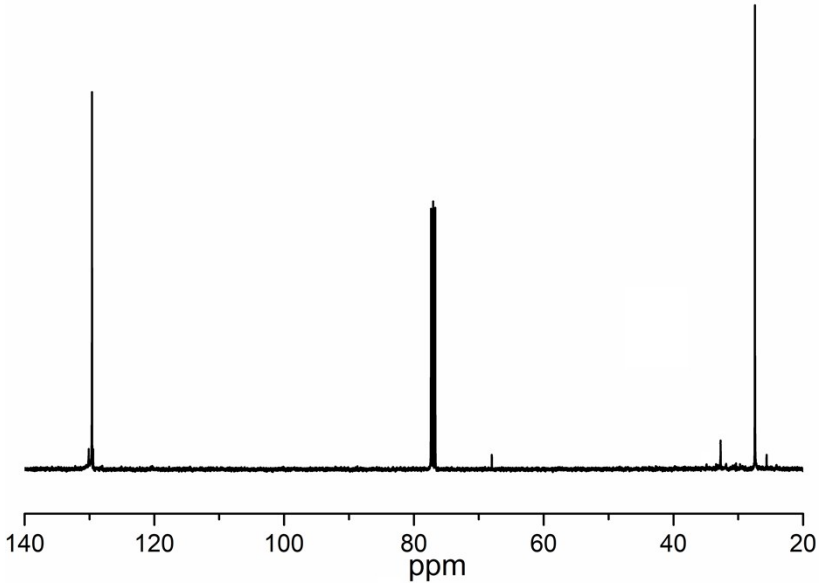

Figure S13 the ^{13}C NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=10:1, Li/B=1:3, 50℃, 4h)

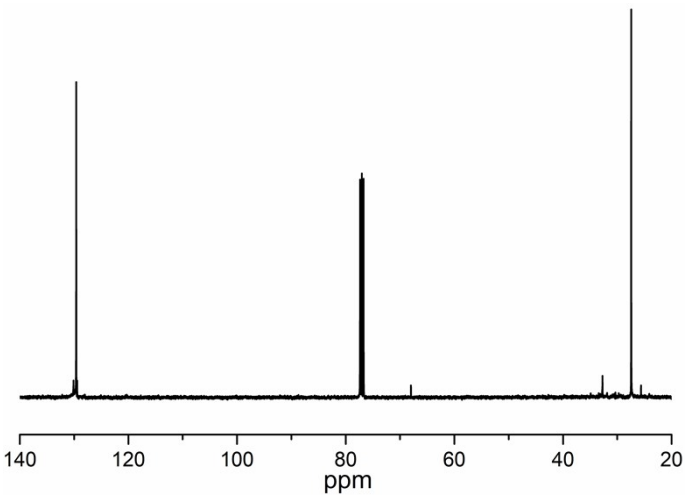

Figure S14 the ^{13}C NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=10:1, Li/B=1:4, 50℃, 4h)

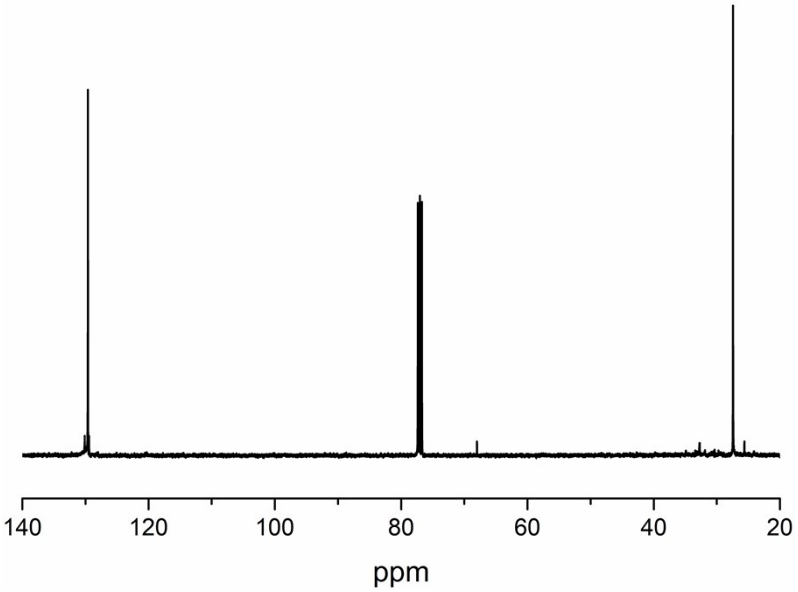

Figure S15 the ^{13}C NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=10:1, Li/B=1:8, 50℃, 4h)

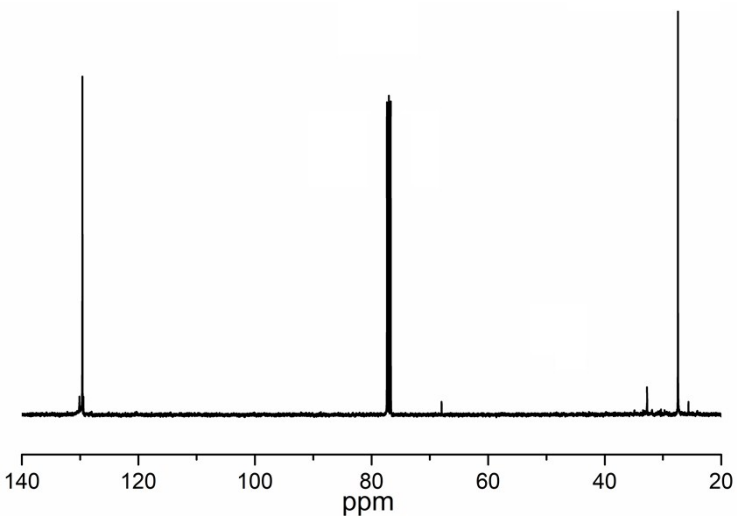

Figure S16 the ^{13}C NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=2.5:1, Li/B=1:2, 50℃, 4h)

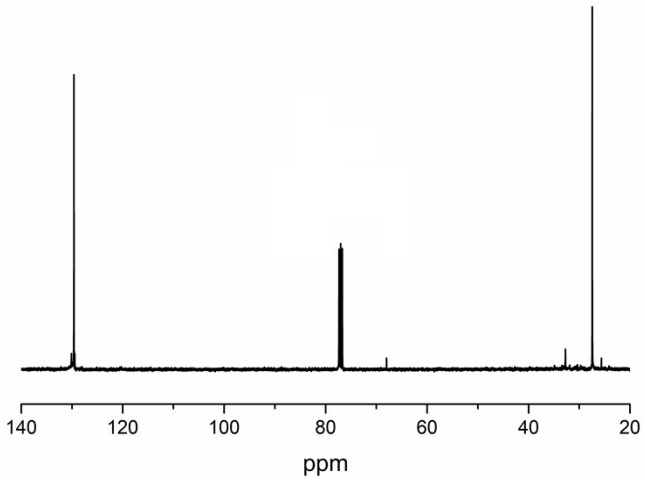

Figure S17 the ^{13}C NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=5:1, Li/B=1:2, 50℃, 4h)

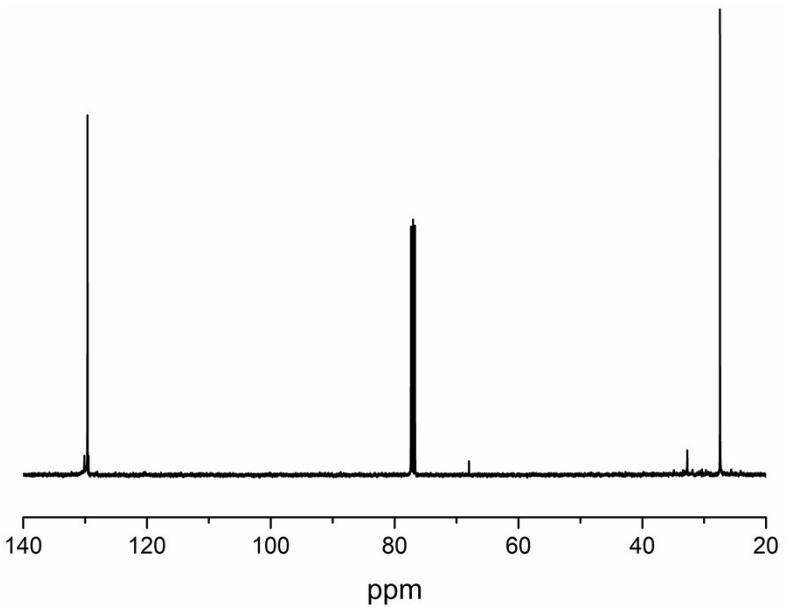

Figure S18 the ^{13}C NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=10:1, Li/B=1:2, 50℃, 4h)

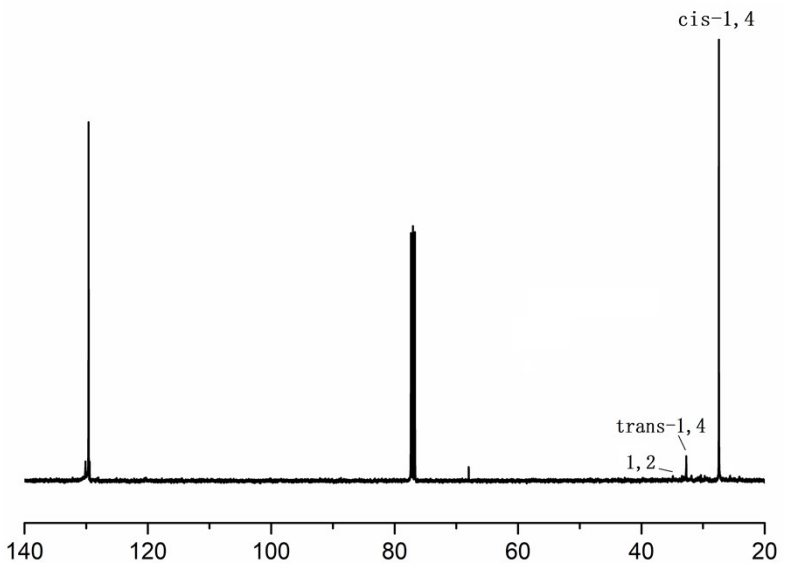

Figure S19 the ^{13}C NMR spectrum of HTPB (polymerization process: nickel naphthenate 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml，Li/Ni=20:1, Li/B=1:2, 50℃, 4h)

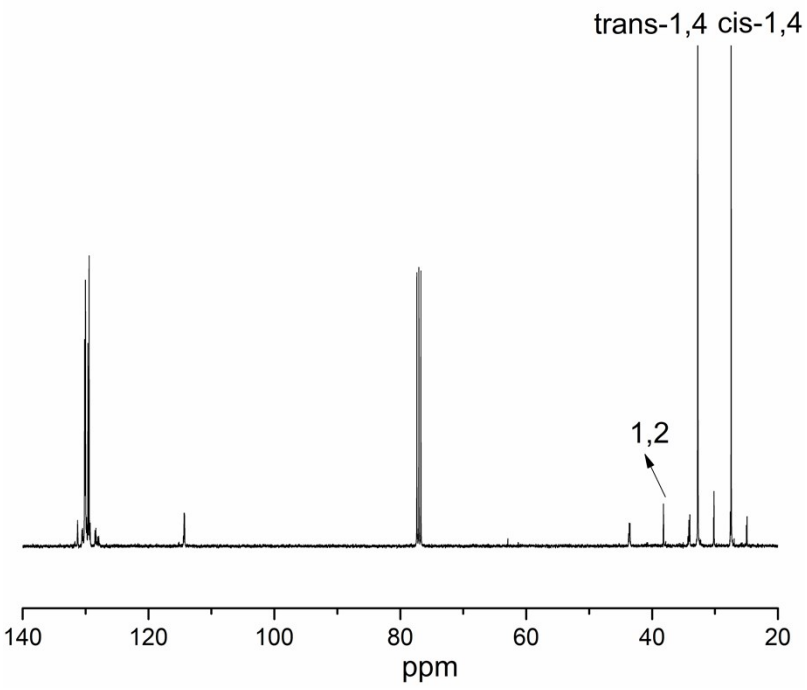

Figure S20 the ^{13}C NMR spectrum of HTPB (polymerization process: Li amount: 2×10^{-5}mol，Bd (15wt%,n-hexane) 10ml， 50℃, 4h)