## Supplementary Information

*Article*

# Controlled and Efficient Polymerization of Conjugated Polar Alkenes by Lewis Pairs Based on Sterically Hindered Aryloxide-Substituted Alkylaluminumitle

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**Table S1.** $M_n$ and $Đ$ results of PMMAs produced by $Al(BHT)_2Me/^{(Ph)Et}NHC$.[a] .

| Time (min) | Conv.(%) | $M_n$ (kg/mol) | $Đ$ |
|---|---|---|---|
| 4 | 17.6 | 22.4 | 1.11 |
| 6 | 33.3 | 43.1 | 1.04 |
| 8 | 46.4 | 52.9 | 1.10 |
| 10 | 62.4 | 69.6 | 1.05 |
| 16 | 100 | 102.7 | 1.06 |

[a] Conditions: $MMA/Al(BHT)_2Me/^{(Ph)Et}NHC$ = 500/2/1.

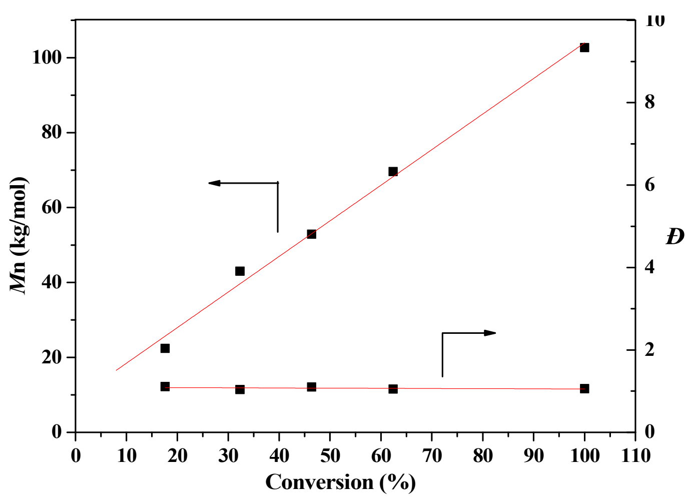


**Figure S1.** Plots of $M_n$ and $Đ$ vs monomer conversion (%) for the MMA polymerization by $^{(Ph)Et}NHC/Al(BHT)_2Me$.

**Table S2.** $M_n$ and $Đ$ results of PMMAs produced by Al(BHT)$_2$Me/$^{iPr}$NHC.[a] .

| Time (min) | Conv.(%) | $M_n$ (kg/mol) | $Đ$ |
|---|---|---|---|
| 4 | 13.2 | 20.2 | 1.09 |
| 6 | 19.2 | 27.6 | 1.13 |
| 10 | 30.8 | 45.1 | 1.09 |
| 16 | 52.4 | 69.5 | 1.08 |
| 20 | 65.5 | 87.6 | 1.09 |
| 25 | 82.8 | 114.8 | 1.06 |
| 30 | 98.0 | 130.6 | 1.07 |

[a] Conditions: MMA/Al(BHT)$_2$Me/$^{iPr}$NHC = 500/2/1.

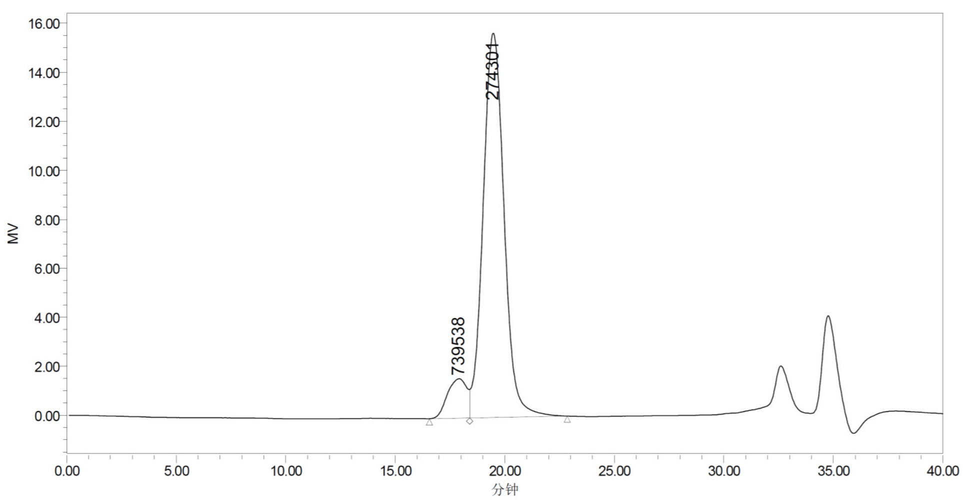


**Figure S2.** GPC trace of PMMA produced by Al(BHT)$_2$Me/$^{tBu}$NHC (Table1, Run 14): $M_n$ = 258.0 kg/mol, $Đ$ = 1.08 (91%); $M_n$ = 786.0 kg/mol, $Đ$ = 1.07 (9%).

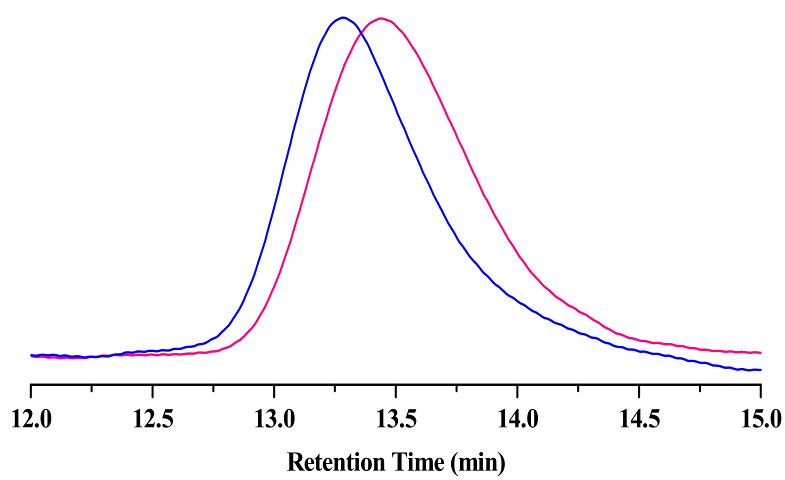


**Figure S3.** GPC trace of PMMA (red) and PMMA-*b*-P$^n$BuMA (blue) produced by Al(BHT)$_2$Me/$^{(Ph)Et}$NHC [$M_n$ and $Đ$ were measured by GPC analyses carried out at 40 ºC and a flow rate of 1.0 mL/min, with DMF as the eluent, on a Waters 2695 GPC instrument equipped with a OPTILAB® T-rEX Interferometric Refractometer detector and PLgel 5 $\mu$m guard and two PLgel 5 $\mu$m mixed-C columns (Agilent, linear range of molecular weight = 200–2,000,000) connected in series. The instrument was calibrated with 10 PMMA standards, and chromatograms were processed with OPTILAB software].

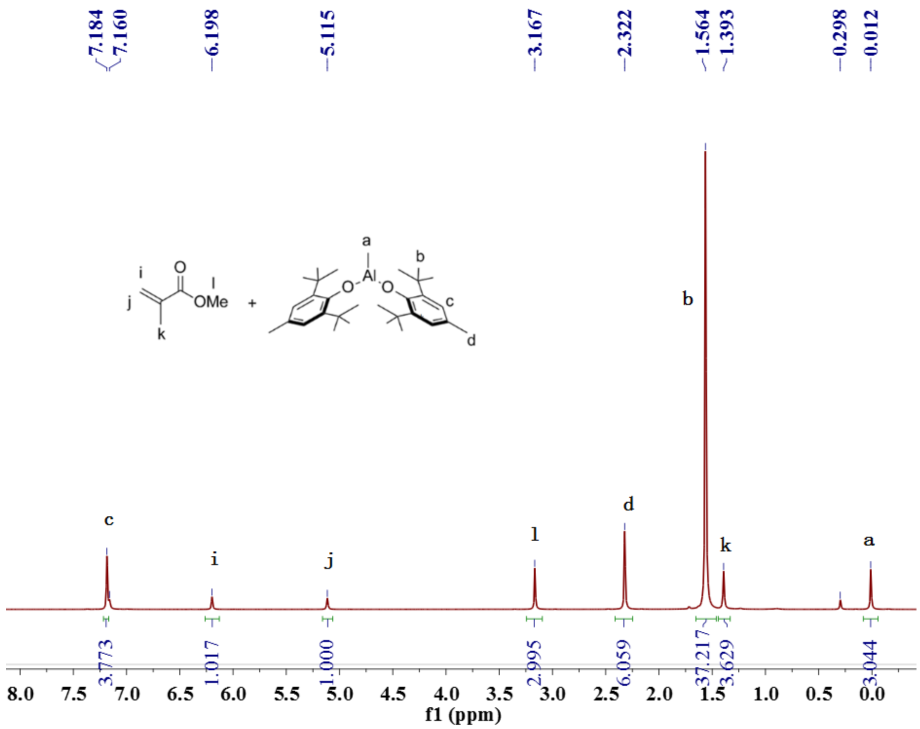


**Figure S4.** [1]H-NMR spectrum of MMA→Al(BHT)$_2$Me adduct in benzene-*d*$_6$.

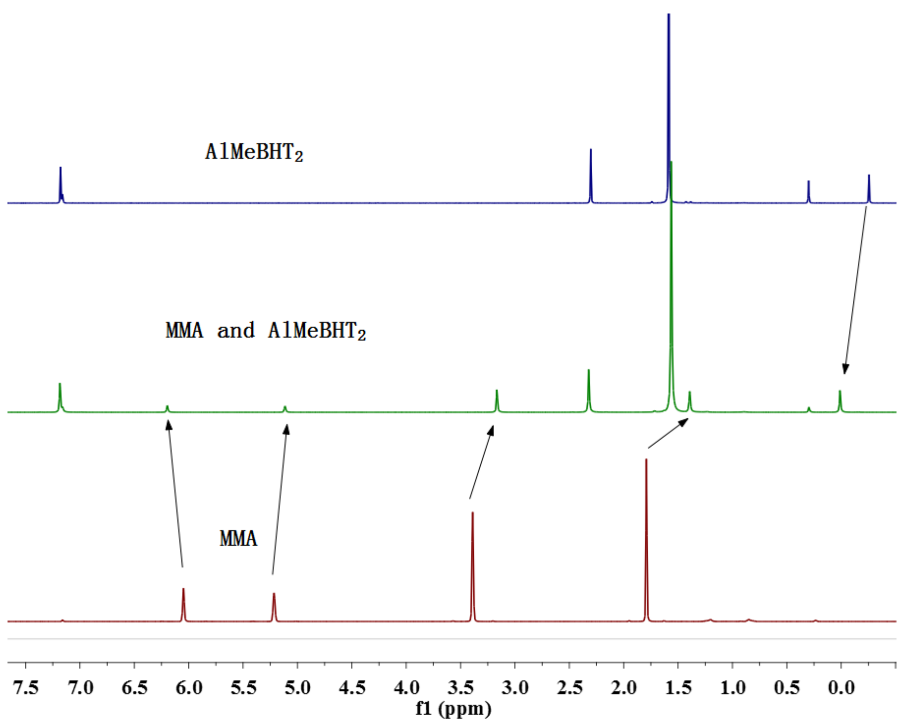


**Figure S5.** Comparison of [1]H NMR spectra in benzene-*d*$_6$: (blue) Al(BHT)$_2$Me, (green) MMA→Al(BHT)$_2$Me adduct, (red) MMA.

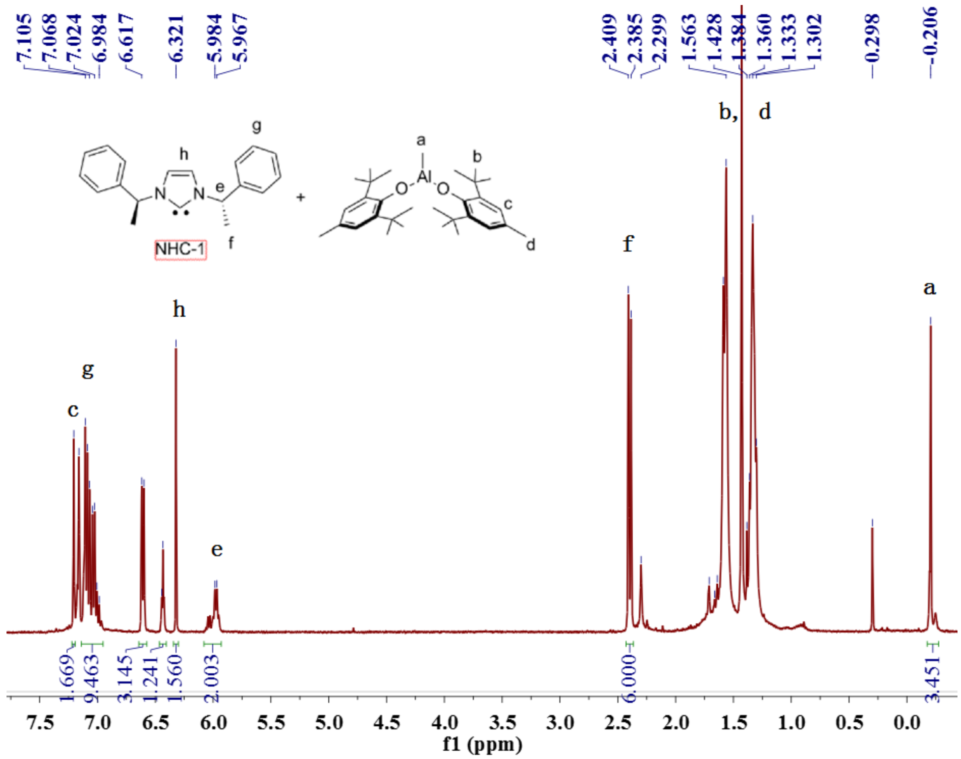


**Figure S6.** [1]H-NMR spectrum of [(Ph)Et]NHC→Al(BHT)$_2$Me adduct in benzene-$d_6$.

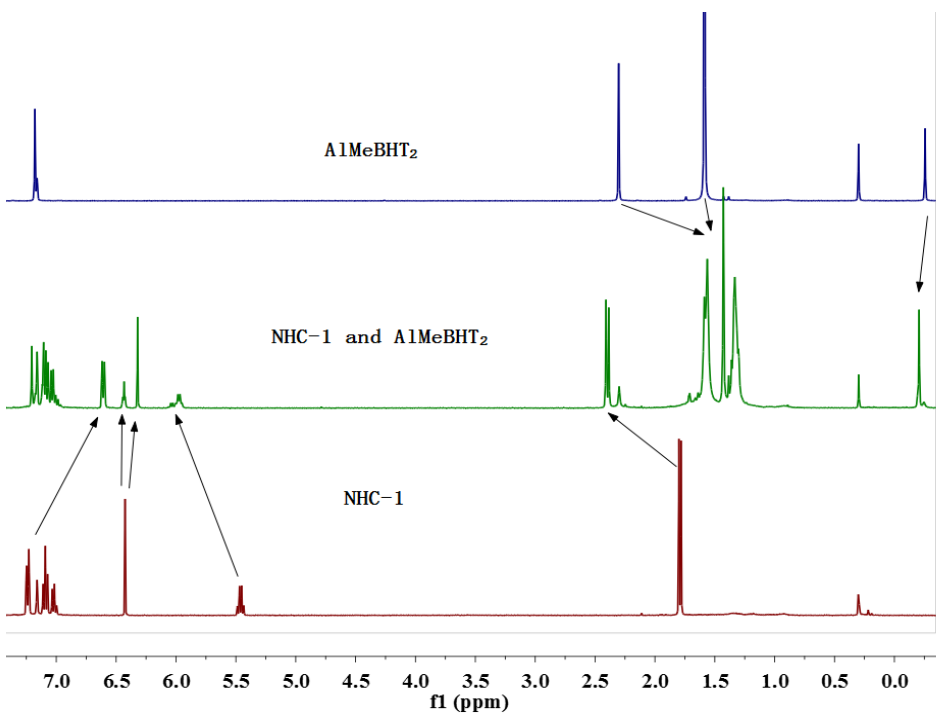


**Figure S7.** Comparison of [1]H NMR spectra in benzene-$d_6$: (blue) Al(BHT)$_2$Me, (green) [(Ph)Et]NHC→Al(BHT)$_2$Me adduct, (red) [(Ph)Et]NHC.

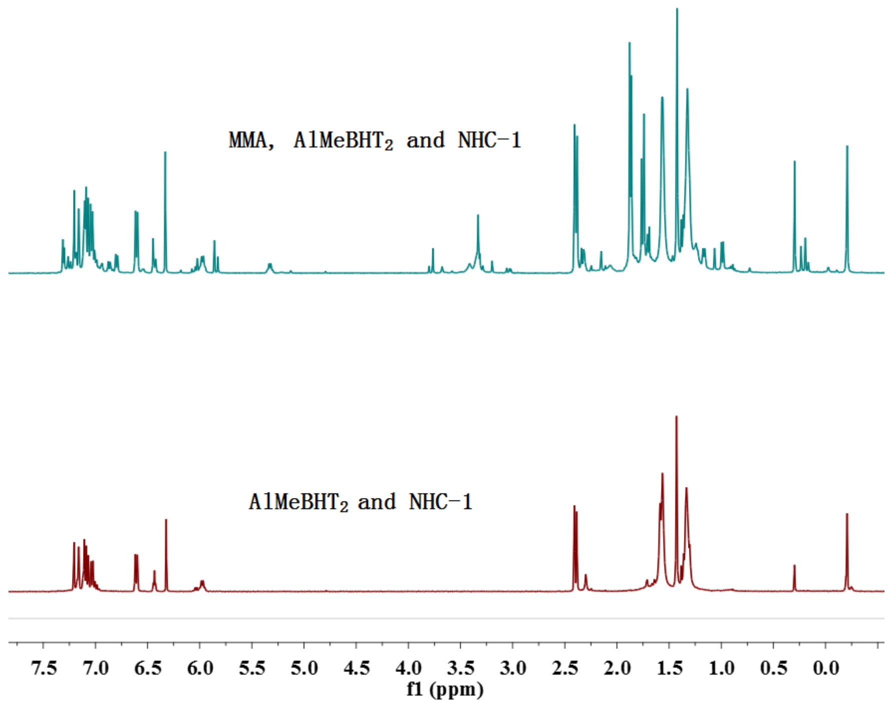


**Figure S8.** Comparison of $^1$H-NMR spectra in benzene-$d_6$: (blue) stoichiometric reaction of $Al(BHT)_2Me$, MMA, and $^{(Ph)Et}$NHC, (red) $^{(Ph)Et}NHC \rightarrow Al(BHT)_2Me$ adduct.