Electronic Supplementary Material (ESI) for Polymer Chemistry.


Supporting Information

# Sequence Regulation in the Living Anionic Copolymerization of Styrene and 1-(4-Dimethylaminophenyl)-1-phenylethylene by Modification with Different Additives

Pibo Liu, Hongwei Ma*, Wei Huang, Li Han, Xinyu Hao, Heyu Shen, Yu Bai and Yang Li*

Liaoning Key Laboratory of Polymer Science and Engineering, Department of Polymer Science and Engineering, State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China.

*E-mail: mahw@dlut.edu.cn (H. Ma), liyang@dlut.edu.cn (Y.Li)

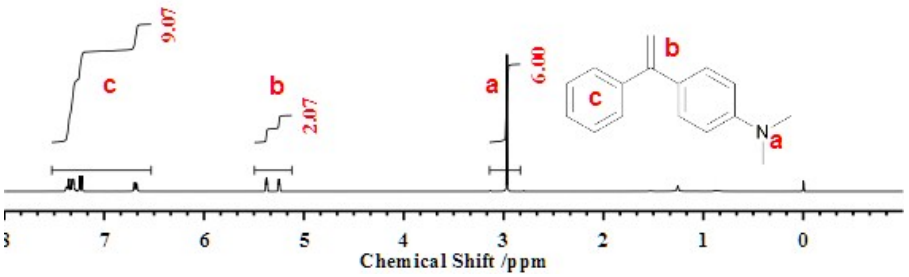


Fig. S1 $^{1}H$ NMR spectra of DPE-$NMe_2$.

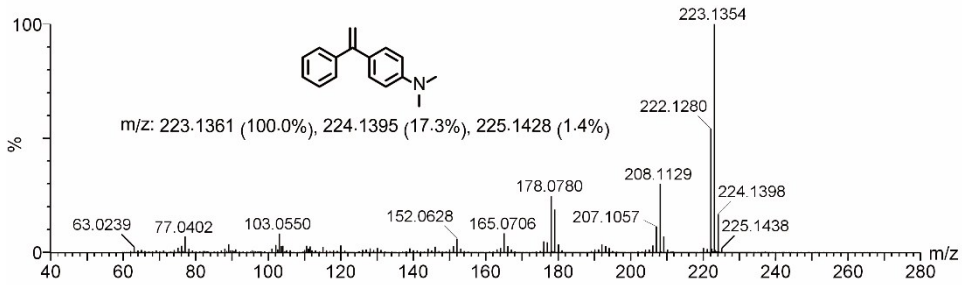


Fig. S2 MS-EI spectrum of DPE-$NMe_2$

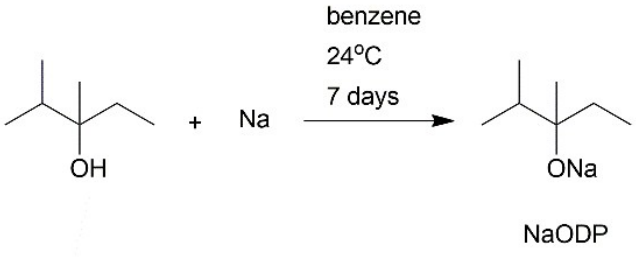


Fig. S3 the synthetic route of NaODP

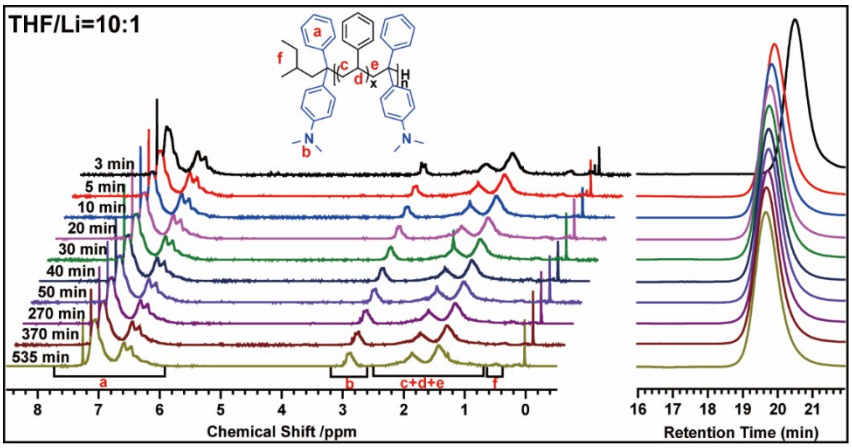


Fig. S4 $^{1}$H NMR spectra and SEC results of copolymerization II under THF condition

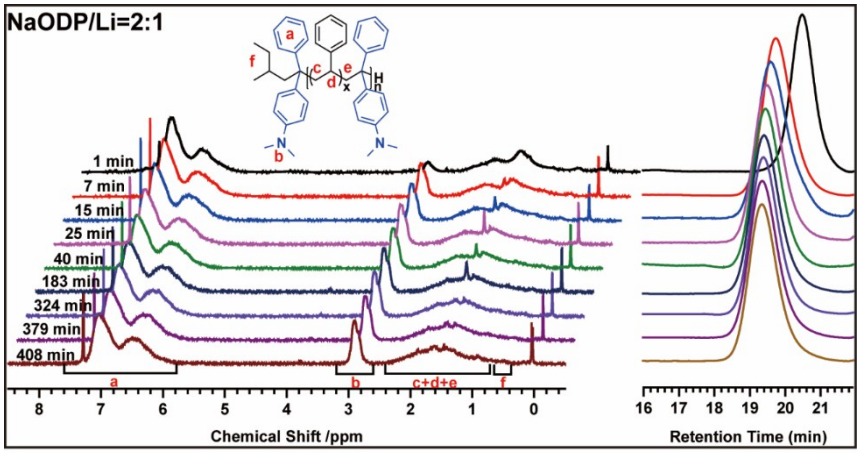


Fig. S5 $^{1}$H NMR spectra and SEC results of copolymerization II under NaODP condition

Table 1S Some timing-sample results for the copolymerization of styrene ($M_{St}$) and DPE-$NMe_2$ ($M_D$)

| Sample[a] | Time (min) | Mn (kg/mol)[b] | PDI[b] | $N_{St}/N_D$[c] | $N_D$[d] | $N_{St}$[d] | Conv.DPE [%][e] | Conv.St [%][f] | $r_{St}$ |
|---|---|---|---|---|---|---|---|---|---|
| I-8 | 115 | 5.8 | 1.20 | 4.6 | 7.9 | 36 | 21.7% | 100.0% | |
| I-9 | 175 | 5.9 | 1.20 | 4.6 | 7.9 | 36 | 21.7% | 100.0% | |
| I-10 | 215 | 5.9 | 1.20 | 4.5 | 8.0 | 36 | 22.2% | 100.0% | 9.1 |
| I-11 | 255 | 5.9 | 1.20 | 4.3 | 8.3 | 36 | 23.3% | 100.0% | |
| I-12 | 415 | 5.9 | 1.20 | 4.2 | 8.5 | 36 | 24.2% | 100.0% | |
| III-6 | 183 | 9.3 | 1.14 | 3.6 | 14.7 | 53 | 27.78% | 100.00% | |
| III-7 | 324 | 9.3 | 1.14 | 3.6 | 14.5 | 53 | 27.78% | 100.00% | 6.9 |
| III-8 | 379 | 9.3 | 1.14 | 3.6 | 14.6 | 53 | 27.78% | 100.00% | |

a. The copolymerization was initiated by *sec*-BuLi at 24 °C in benzene, and the feed ratio of St to DPE-$NMe_2$ was $N_{St}/N_D$=1. In addition, the concentration of the species was $3.0\times10^{-3}$ mol/L.

b. Determined by SEC.

c. The composition ratio of $N_{St}$ to $N_D$ of the polymers was calculated from the $^{1}$H NMR spectra.

d. The average number of DPE units in each polymer chain was calculated from the $^{1}$H NMR spectra and SEC.

e. The relative conversion of DPE-$NMe_2$.

f. The relative conversion of St.