

## Electronic Supplementary Information

# **Stereoselective copolymerization of (N,N-diphenylamino)styrene and isoprene by a C<sub>5</sub>H<sub>5</sub>-ligated scandium catalyst: synthesis of amino-functionalized crystalline styrenic thermoplastic elastomers**

*Fang Guo,<sup>a</sup> Lei Jiang,<sup>a</sup> Kaiying Diao,<sup>a</sup> Zhaomin Hou<sup>a,b,c</sup>*

<sup>a</sup> State Key Laboratory of Fine Chemicals, Department of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116012, China

<sup>b</sup> Organometallic Chemistry Laboratory, RIKEN Cluster for Pioneering Research, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

<sup>c</sup> Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

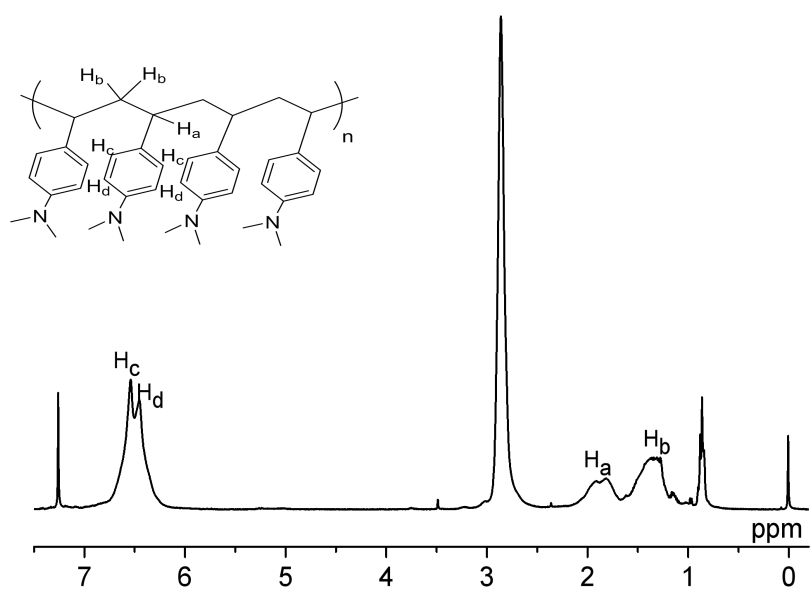


Fig. S1  $^1\text{H}$ -NMR spectrum of a DMAS polymer prepared by  $(\text{C}_5\text{H}_5)\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_2/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in chloroform-*d* at room temperature

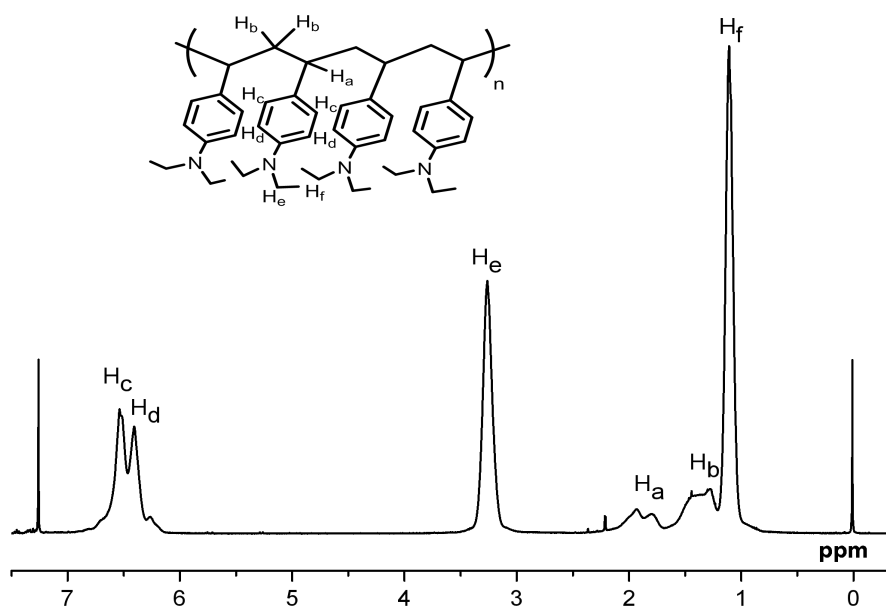


Fig. S2  $^1\text{H}$ -NMR spectrum of a DEAS polymer prepared by  $(\text{C}_5\text{H}_5)\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_2/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in chloroform-*d* at room temperature

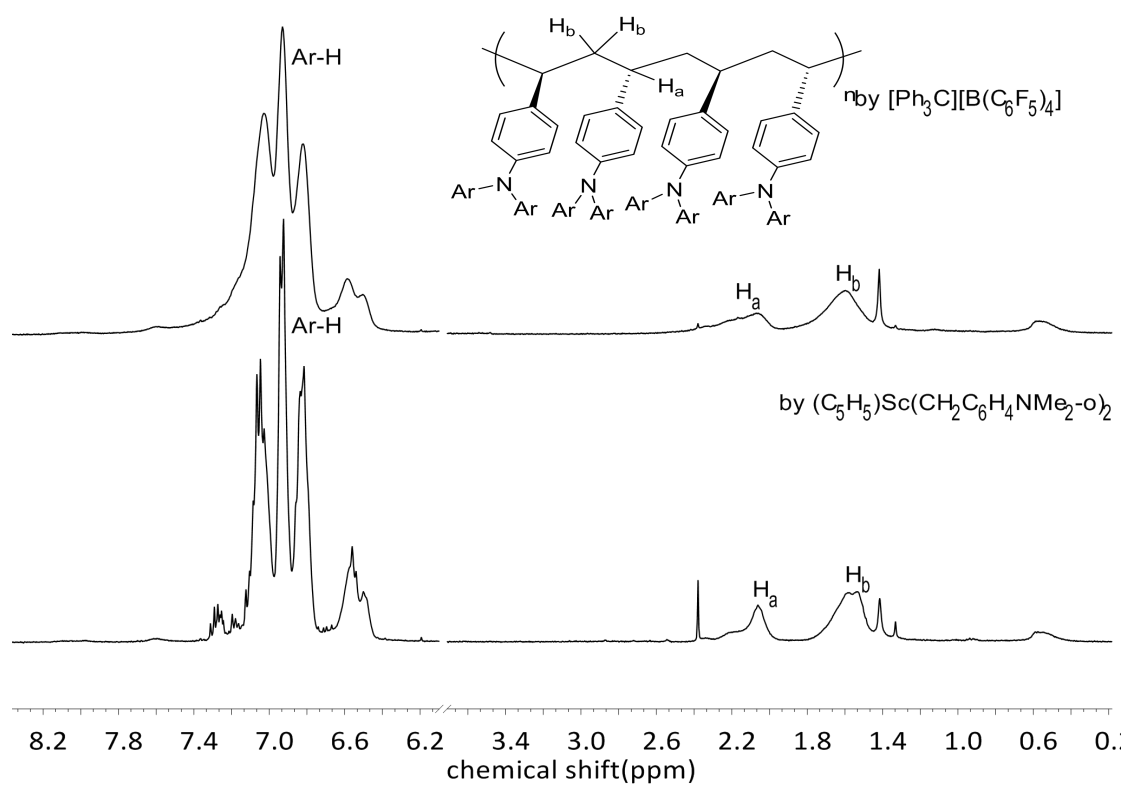


Fig. S3  $^1\text{H-NMR}$  spectra of a DPAS polymer prepared by  $(\text{C}_5\text{H}_5)\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})_2/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  or  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in chloroform-*d* at room temperature

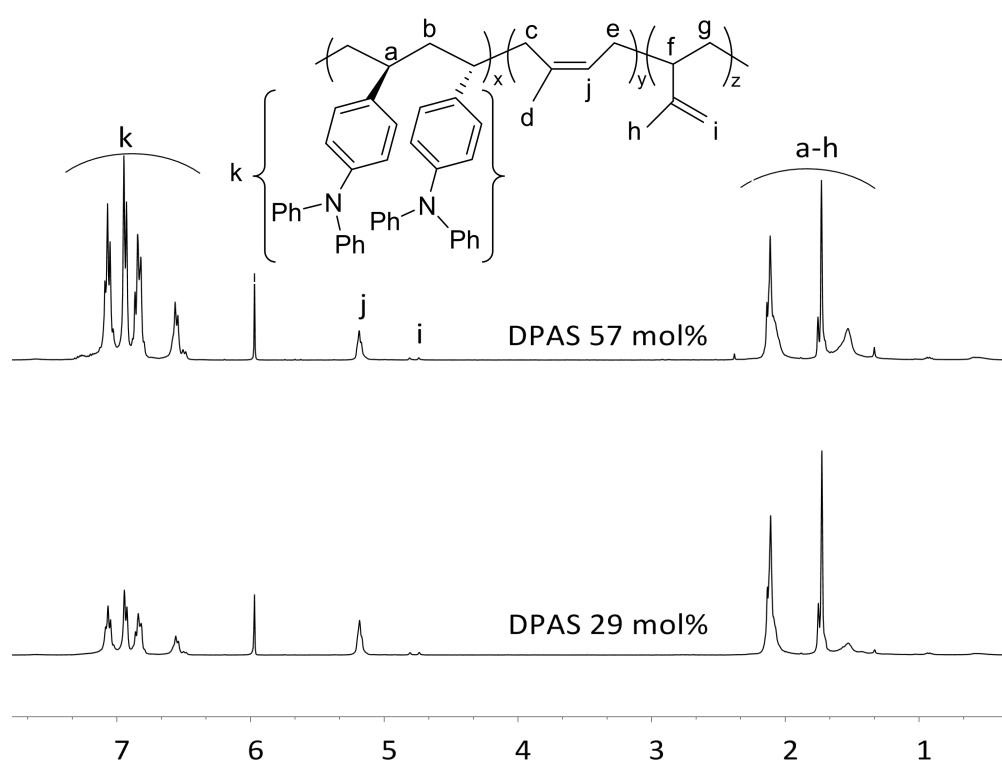
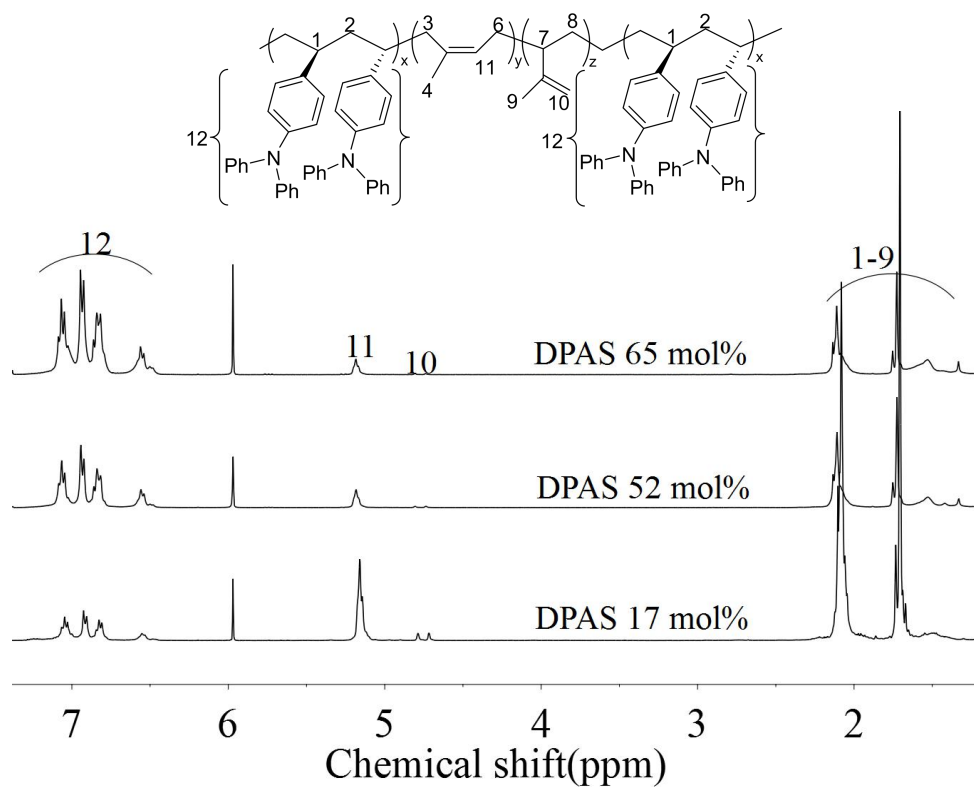
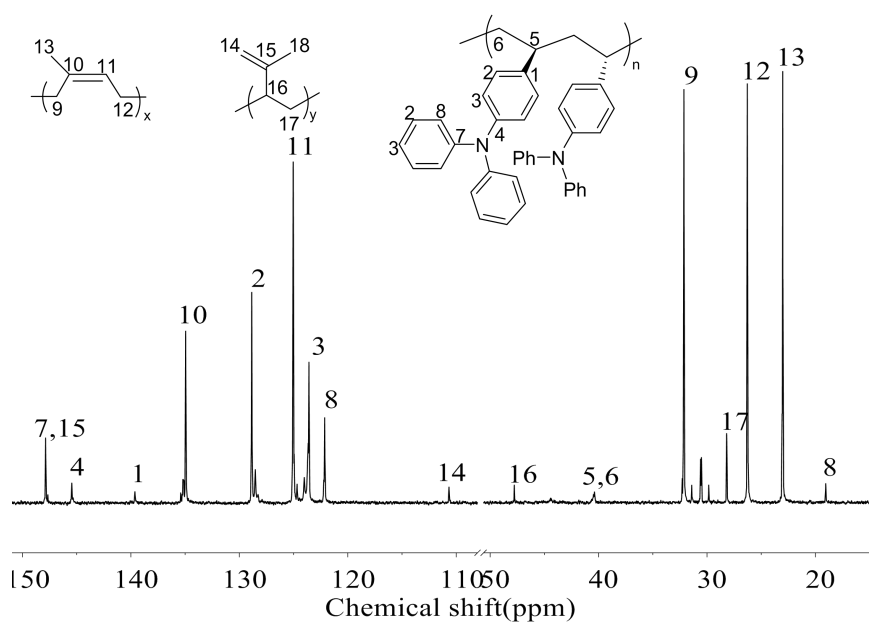


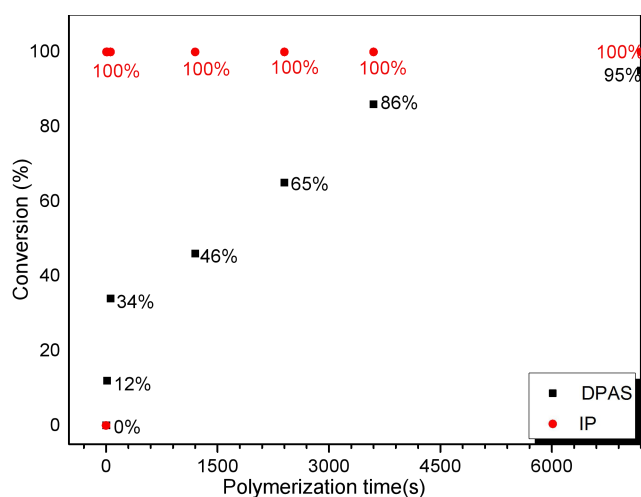
Fig.S4  $^1\text{H-NMR}$  spectra of DPAS-IP copolymers with different composition prepared by  $(\text{C}_5\text{H}_5)\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})_2/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> at 110 °C



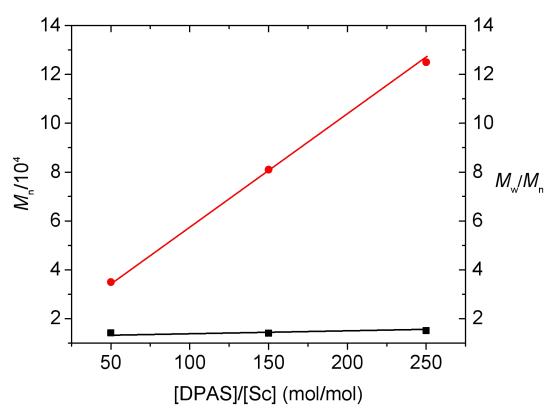
**Fig.S5**  $^1\text{H}$ -NMR spectra of DPAS-IP-DPAS terpolymers with different composition prepared by  $(\text{C}_5\text{H}_5)\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_2/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in 1,1,2,2-tetrachloroethane- $d_2$  at 110  $^\circ\text{C}$



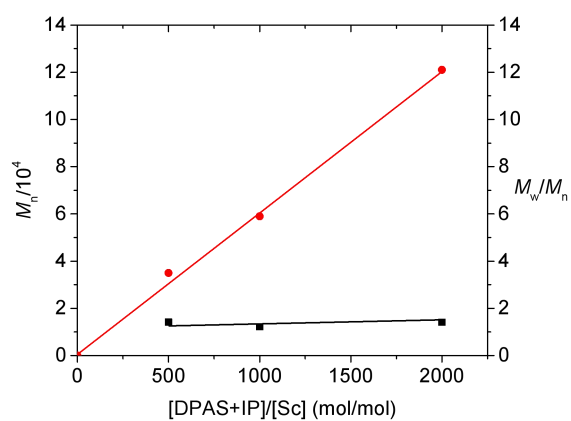
**Fig.S6**  $^{13}\text{C}$ -NMR spectrum of a DPAS-IP-DPAS terpolymer prepared by  $(\text{C}_5\text{H}_5)\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_2/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in 1,1,2,2-tetrachloroethane- $d_2$  at 110  $^\circ\text{C}$



**Fig. S7** Plots of the conversions of DPAS (black) and IP (red) versus the polymerization time.



**Fig. S8** Plots of  $M_n$  and  $M_w/M_n$  as a function of the DPAS/catalyst ratio for DPAS-IP copolymerization.



**Fig. S9** Plots of  $M_n$  and  $M_w/M_n$  as a function of the [DPAS+IP]/catalyst ratio for DPAS-IP copolymerization.