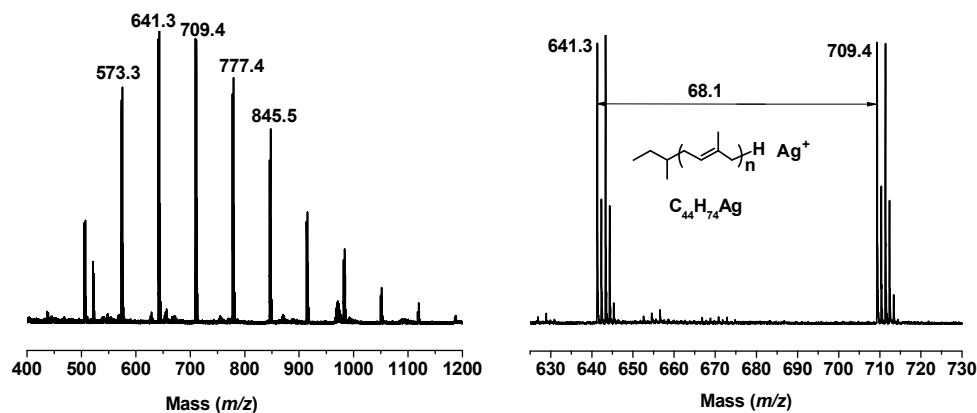


## Supporting Information

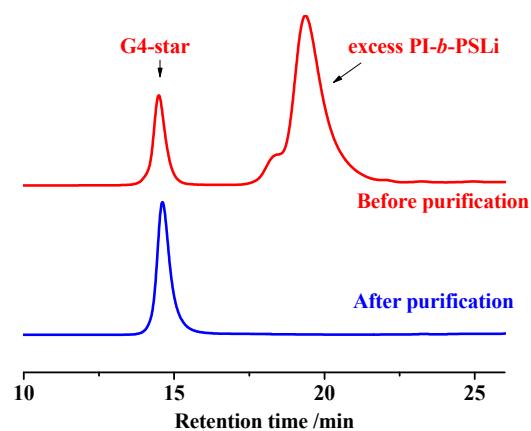
### Easy Synthesis of Dendrimer-like Polymers through A Divergent Iterative “End-grafting” Method

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**Fig. S1** MALDI-TOF MS spectrum of the PI oligomer used as the branching unit.

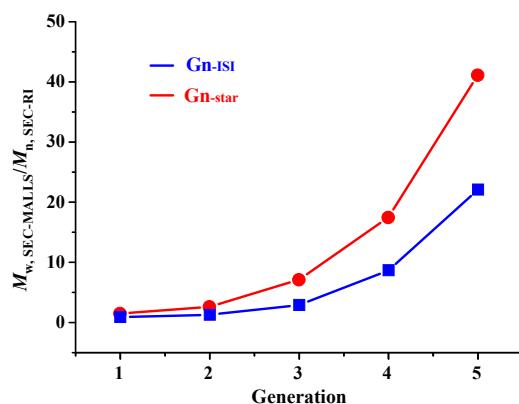


**Fig. S2** SEC curves of dendrimer-like PS G4<sub>star</sub> before and after purification.

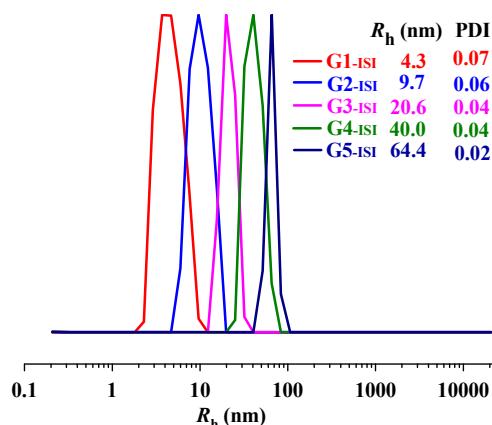
**Table S1** Viscosities and contraction factor of the dendrimer-like PS

Entry	$M_w (\times 10^3 \text{ g/mol})$	$[\eta]_{\text{linear theo.}} (\text{ml/g})^{\text{a}}$	$[\eta]_{\text{dendrimer-like}} (\text{ml/g})^{\text{b}}$	$g'{}^{\text{c}}$
<b>G1-ISI</b>	29.4	20.4	19.4	0.95
<b>G2-ISI</b>	169	71.04	33.6	0.47
<b>G3-ISI</b>	1242	295.0	43.6	0.15
<b>G4-ISI</b>	7512	1066.3	45.0	0.04
<b>G5-ISI</b>	36270	3281.8	37.2	0.01
<b>G1-star</b>	50.1	29.8	16.1	0.54
<b>G2-star</b>	343	117.7	25.6	0.22
<b>G3-star</b>	2230	448.0	32.0	0.07
<b>G4-star</b>	10340	1339.6	32.5	0.02
<b>G5-star</b>	40770	3567.6	30.8	0.01

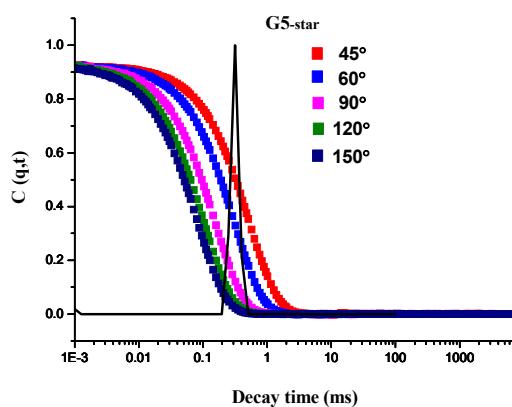
<sup>a</sup>  $[\eta]_{\text{linear, theo.}}$  was calculated according to  $[\eta]_{\text{linear, theo.}} = 1.314 \times 10^{-2} M_w^{0.714}$  (G. Meyerhoff and B. Appelt, *Macromolecules*, 1979, **12**, 968); <sup>b</sup> Measured at 30°C in THF; <sup>c</sup>  $g' = [\eta]_{\text{dendrimer-like}} / [\eta]_{\text{linear, theo.}}$



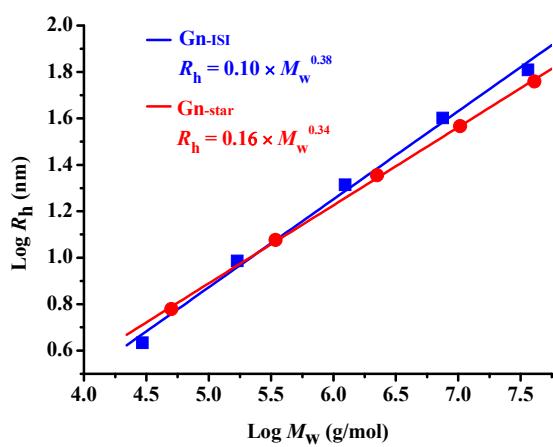
**Fig. S3** Ratios of  $M_w, \text{SEC-MALLS}$  to  $M_n, \text{SEC-RI}$  of **Gn-ISI** and **Gn-star** as a function of generation number.



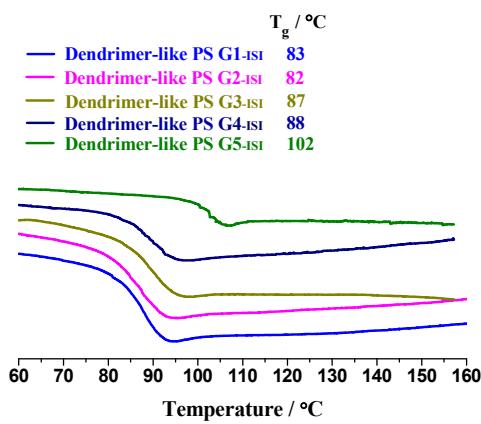
**Fig. S4**  $R_h$ s of the dendrimer-like PS **Gn-ISI** increase with generations.



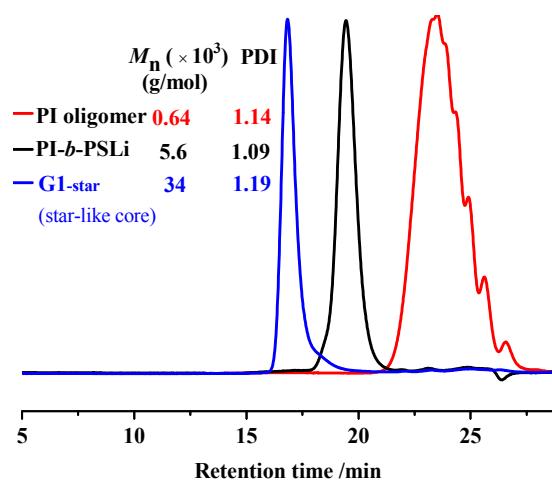
**Fig. S5** DLS results of dendrimer-like star polystyrenes of **G5<sub>star</sub>** at different angles (in THF), showing no angle dependence in molecular size measurement.



**Fig. S6** Relationships between  $\langle R_h \rangle$  and  $M_w$  in a log-log scale.



**Fig. S7** DSC results for dendrimer-like products of **Gn\_ISI** where n = 1–5.



**Fig. S8** SEC monitoring the synthetic process of the star-like core.