## Effects of Molecular Geometry on the Self-Assembly of Giant Polymer-Dendron Conjugates in Condensed State

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Figure S1. SEC chromatograms of  $PS_N$  with different degree of polymerization (see Table 1).



**Figure S2.** Typical <sup>1</sup>H NMR spectrum of  $PS_N$ -Br prepared *via* ATRP. The results are based on the samples with N = 19.



**Figure S3.** FT-IR spectra of  $PS_N$ -N<sub>3</sub> (red) and  $PS_N$ -*t*D (blue). The results are based on the samples with N = 19.



**Figure S4.** <sup>13</sup>C NMR spectra of (a) Alkyne Functionalized, *t*-Butyl-protected Dendron; (b)  $PS_N tD$ ; and (c)  $PS_N D$ . The results are based on the samples with N = 19.



**Figure S5.** Small angle X-ray scattering pattern (a, c) and TEM bright field image (b, d) of  $PS_{80}$ -*t*D and  $PS_{150}$ -D, respectively. The scale bar is 50 nm.



**Figure S6.** Temperature dependent SAXS patterns for PS<sub>16</sub>-D, Lam (*a*); PS<sub>24</sub>-D, DG (*b*); PS<sub>30</sub>-D, Hex (*c*); and PS<sub>90</sub>-D, BCC (*d*).



Figure S7. Temperature dependence of density of alkyne-functionalized dendron (Alkyne-D).



Figure S8. Temperature dependence of density of polystyrene.

 $PS_{16}$ -D *PS*<sub>24</sub>-*D PS*<sub>60</sub>-*D*  $PS_{82}$ -D  $PS_{19}$ -D PS<sub>28</sub>-D *PS*<sub>35</sub>-*D* PS<sub>80</sub>-D  $PS_{91}$ -D  $PS_{150}$ -D 20 °C 0.65236 0.69025 0.73786 0.76657 0.80411 0.87558 0.90369 0.90581 0.91433 0.94622 40 °C 0.653 0.76708 0.87588 0.90606 0.69085 0.73841 0.80456 0.90393 0.91455 0.94636 60 °C 0.65367 0.69149 0.76761 0.80502 0.87621 0.73898 0.90419 0.90631 0.91478 0.94651 80 °C 0.65442 0.69219 0.73962 0.7682 0.80554 0.87656 0.90448 0.90659 0.91504 0.94668 100 °C 0.65523 0.69295 0.74031 0.76883 0.8061 0.87695 0.90689 0.90478 0.91532 0.94686 140 °C 0.65703 0.69464 0.74184 0.77024 0.80734 0.87781 0.90547 0.90756 0.91593 0.94726 180 °C 0.65909 0.69658 0.74359 0.77186 0.80876 0.87879 0.90625 0.90833 0.91664 0.94771

Table S1. Temperature dependence of volume fraction  $f_{PS}$ .