# 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 $\mathrm{PS}_{N}$ with different degree of polymerization (see Table 1).


Figure S2. Typical ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathrm{PS}_{N}-\mathrm{Br}$ prepared via ATRP. The results are based on the samples with $N=19$.


Figure S3. FT-IR spectra of $\mathrm{PS}_{N}-\mathrm{N}_{3}$ (red) and $\mathrm{PS}_{N}-t \mathrm{D}$ (blue). The results are based on the samples with $N=19$.


Figure S4. ${ }^{13} \mathrm{C}$ NMR spectra of (a) Alkyne Functionalized, $t$-Butyl-protected Dendron; (b) $\mathrm{PS}_{N^{-}} t \mathrm{D}$; and (c) $\mathrm{PS}_{N}$-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 $\mathrm{PS}_{80}-t \mathrm{D}$ and $\mathrm{PS}_{150}-\mathrm{D}$, respectively. The scale bar is 50 nm .


Figure S6. Temperature dependent SAXS patterns for $\mathrm{PS}_{16}-\mathrm{D}$, Lam (a); $\mathrm{PS}_{24}-\mathrm{D}, \mathrm{DG}(b) ; \mathrm{PS}_{30}-\mathrm{D}$, Hex (c); and $\mathrm{PS}_{90}-\mathrm{D}, \mathrm{BCC}(d)$.


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


Figure S8. Temperature dependence of density of polystyrene.

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

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

