SUPPORTING INFORMATION

Rheology and packing of dendronized polymers

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S1. Supplementary procedure for quantification of structure perfection

**Scheme S1.** Schematic representation of the UV-labeling reaction of unreacted amines (defect sites) using 1-fluoro-2,4-dinitrobenzene (Sanger’s reagent).

**Sample preparation:**

The UV-labelled DP samples were prepared by a previously reported procedure\(^1\), as exemplified for the PG3-3000 sample: PG3-3000 (16.8 mg) was weighed in a 10 ml round bottom flask and dissolved in 1,1,2,2-tetrachloroethane (0.23 mL). After addition of NaHCO\(_3\) (0.1 M solution, 0.29 mL) and Sanger’s reagent (2.86 mg in 0.36 mL 1,1,2,2-tetrachloroethane, 0.3 equiv per amino group), the flask was sealed with a rubber sept and the reaction mixture was heated to 65 °C for 3 h with stirring. After cooling to room temperature, the reaction mixture was diluted with CH\(_2\)Cl\(_2\) (5 mL) and successively washed with saturated Na\(_2\)CO\(_3\) solution (5 mL), water (5 mL) and brine (5 mL). After concentration of the organic layer *in vacuo*, the residue was dissolved in a minimum amount of CH\(_2\)Cl\(_2\) and precipitated into Et\(_2\)O. The precipitation step was repeated twice. After freeze-drying from 1,4-dioxane, 2,4-dinitroaniline-labeled PG3 (8.3 mg, 49%) was obtained as a slightly yellow foam.
Quantification of dendronization:

The quantitative UV experiments were performed on a UV-670 UV/Vis spectrophotometer from JASCO by using 10 mm quartz cuvettes. The UV-labelled polymers were dissolved in 1,1,2,2-tetrachloroethane with concentrations of about $2.641 \times 10^{-4}$ mol/L (repeat unit). The extinction coefficient of 2,4-dinitroaniline moiety ($\varepsilon = 1.64 \times 10^{4}$ L·mol$^{-1}$·cm$^{-1}$) was taken from a previous report$^1$. The concentration of the dinitroanilino moieties, which is also considered as the concentration of unconverted terminal amino groups (supposing all the unreacted amino groups in the dendronization were labeled by treating with Sanger’s reagent), was calculated according to the Lambert-Beer law (Equation 1):

$$c = \frac{A}{\varepsilon \cdot l}$$

(1)

In this equation, $l$ denotes the inside width of the UV cuvettes (1.0 cm) and $A$ denotes the absorption at 357 nm. The structure perfection $X$ for the conversion from $de$-PG2 to PG3 was therefore calculated as $X = (1-c/c_0) \times 100\%$, in which $c$ denotes the concentration of 2,4-dinitroanilino moieties, and $c_0$ denotes the concentration of total termini in the starting material ($de$-PG2), which, e.g. for PG2, is 4 times of the molar concentration of PG3. The UV-Vis spectra of (un)labeled PG2-2000, PG2-3000, PG3-2000, PG3-3000 are shown in Figure S1 (a, b). The results for the degree of coverage (i.e. the perfection of the dendronization) $X$ were calculated from the absorption of labeled dendronized polymers at 357 nm and are summarized in Table S1:
### Table S1. Summarized results of the DP labeling experiments.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>$c$ [mol/L]</th>
<th>$c_0$ [mol/L]</th>
<th>$A$ (at 357 nm)</th>
<th>$X$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PG2-2000</td>
<td>$5.9756 \times 10^{-7}$</td>
<td>$4.3276 \times 10^{-4}$</td>
<td>0.0098019</td>
<td>99.8</td>
</tr>
<tr>
<td>2</td>
<td>PG2-3000</td>
<td>$3.8292 \times 10^{-7}$</td>
<td>$6.6002 \times 10^{-4}$</td>
<td>0.0062827</td>
<td>99.9</td>
</tr>
<tr>
<td>3</td>
<td>PG3-2000</td>
<td>$5.8159 \times 10^{-6}$</td>
<td>$8.6559 \times 10^{-4}$</td>
<td>0.0953810</td>
<td>99.3</td>
</tr>
<tr>
<td>4</td>
<td>PG3-3000</td>
<td>$6.4256 \times 10^{-7}$</td>
<td>$9.1426 \times 10^{-4}$</td>
<td>0.0105380</td>
<td>99.9</td>
</tr>
</tbody>
</table>

**Figure S1.** UV-Vis spectra of unlabeled (black) and labeled (red, $P_n \approx 2000$; blue, $P_n \approx 3000$) DPs. a) PG2. b) PG3.
Scheme S2. Reagents and Conditions: (i) LiAlH₄, THF, -20 °C, 4 h; (ii) MAC, Et₃N, DMAP, CH₂Cl₂, -10 °C, 2.5 h; (iii) AIBN, (CDB), DMF, 65 °C, 13-24 h; (iv) TFA, -10 °C to room temperature, overnight; (v) Et₃N, DMAP, DMF, room temperature, 4-12 d.
**Materials:** Unless noted otherwise, all reactions were carried out in dried Schlenk glassware, in dried solvents and in an inert nitrogen atmosphere. For reactions, the used solvents were of analytical grade and obtained from a solvent purification system by LC Technology Solutions Inc., Seabrook, NH. Chromatography solvents were purchased as technical grade and distilled once prior to use. Methacryloyl chloride (MAC) was purchased from Sigma-Aldrich (97%) and freshly distilled before use. Azobis(isobutyronitrile) (AIBN) was purchased from Fluka-Chemie AG (>98%) and recrystallized from methanol. All other chemicals were commercially obtained as reagent grade and used without further purification. Methyl ester 1a and the succinimidyl ester 1d were purchased from Synwit Technology Co. (both >95%), 2-phenyl-2-propyl benzodithioate (CDB, 99%) and triethylamine (>99%) were purchased from Sigma-Aldrich, 4-dimethylaminopyridine (DMAP, 99%) and lithium aluminiumhydride (2.4 M in THF) were purchased from Acros Organics. TLC analyses were performed on pre-coated aluminum sheets (silica gel 60G/UV254, 0.20 mm) from Macherey-Nagel. UV-light (254 nm) was used for detection. Column chromatography was conducted on silica gel 60 Å from Fluka (230-400 mesh particle size) as the stationary phase.

**Characterization:** $^1$H and $^{13}$C NMR spectroscopy was performed on a Bruker AV 300 ($^1$H, 300 MHz; $^{13}$C, 75 MHz) spectrometer at room temperature. Polymer spectra were recorded at 340 K to improve NMR resolution. Chemical shifts are reported as $\delta$ values (ppm) and were calibrated according to residual protons in CDCl$_3$ (7.26 ppm). High-resolution ESI-Qq-TOF-MS (Bruker maXis; solvent, CH$_2$Cl$_2$/MeOH; ion polarity, positive; set capillary, 4500.0 V) and ESI/MALDI-FTICR-MS (Bruker solariX 94; matrix, THA; solvent, CH$_2$Cl$_2$/MeOH); ion polarity, positive; set capillary, 4500.0 V) analyses were performed by the Service for Mass Spectrometry of the Laboratory of Organic Chemistry (LOC) at ETH Zurich. Elemental analysis
was carried out on a Perkin-Elmer EA 240 by the Micro-Laboratory of the LOC at ETH Zurich after drying of samples in high vacuum (HV) to constant weight.

3-5-Bis[3-(tert-)butyloxy carbonylamino]propyloxy]-benzyl alcohol (1b): Methyl ester 1a (1.00 equiv, 30.0 g, 62.3 mmol) was dissolved in THF (400 ml) and the mixture was cooled to -20 °C. A 2.4 M solution of LiAlH₄ in THF (2.05 equiv, 53.0 ml, 127 mmol) was diluted with THF (120 ml) and added drop wise over 4 h, after which TLC (EtOAc/hexane 1:2) confirmed the consumption of the starting material. The reaction was quenched by the sequential addition of water (4.82 ml), 15% aqueous NaOH solution (4.82 ml) and H₂O (14.5 ml), followed by continued stirring at room temperature overnight. After filtration, CH₂Cl₂ (300 ml) was added and the solution was washed once with saturated aqueous NaHCO₃ solution (100 ml) and once with saturated aqueous NaCl solution (100 ml). After evaporation of the solvents, the oily residue was dissolved in a minimum amount of EtOAc and precipitated into hexane. The precipitate was collected by filtration and dried in vacuo to yield the desired product (25.72 g, 86%) as a colorless solid. 

1H NMR (300 MHz, CDCl₃) δ = 6.51 (d, J = 2.1 Hz, 2H, 2 aromatic H), 6.35 (t, J = 2.1 Hz, 1H, aromatic H), 4.77 (s, 2H, 2 NH), 4.61 (s, 2H, CH₂OH), 3.99 (t, J = 6.0 Hz, 4H, 2 CH₂CHO), 3.30 (q, J = 5.9 Hz, 4H, 2 CH₂CH₂NH), 1.95 (m, 5H, OH, 2 CH₂CH₂CH₂), 1.43 (s, 18H, 2 C(CH₃)₃). 13C NMR (76 MHz, CDCl₃) δ = 160.1 (2 aromatic C), 156.0 (2 C=O), 143.5 (aromatic C), 105.3 (2 aromatic C), 100.6 (aromatic C), 79.2 (2 C(CH₃)₃), 65.8 (CH₂OH), 65.2 (2 CH₂CH₂O), 38.0 (2 CH₂CH₂NH), 29.5 (2 CH₂CH₂CH₂), 28.4 (2 C(CH₃)₃). HRMS (MALDI-TOF, 3-HPA): calcd for C₂₃H₃₈N₂NaO₇ ([M+Na]+) 477.2577; found 477.2571. Rf: 0.10 (hexane/EtOAc 2:1).
3-5-Bis[3-(tert-butoxy carbonylamino) propoxy]-benzyl methacrylate (1c): Benzyl alcohol 1b (1.00 equiv, 24.0 g, 52.9 mmol) was added to CH₂Cl₂ (270 ml), Et₃N (3.01 equiv, 22.2 ml, 159 mmol) and DMAP (0.03 equiv, 219 mg, 1.79 mmol). After cooling of the mixture to -10 °C, a solution of MAC (1.50 equiv, 7.63 ml, 79.4 mmol) in CH₂Cl₂ (50 ml) was added drop wise. After stirring for 2.5 h in cold, the reaction was quenched and washed with saturated aqueous NaHCO₃ solution (2 × 200 ml) and saturated aqueous NaCl solution (100 ml). The organic layer was dried over MgSO₄, filtered and the solvent was removed in vacuo. Purification of the thus obtained, yellowish oil by column chromatography (silica gel, 25 cm, ≈ 400 g, gradient hexane/EtOAc 3:1 → 1:1) yielded the desired product (26.0 g, 94%) as a white solid. 

$$^1$$H NMR (300 MHz, CDCl₃) δ = 6.50 (d, J = 2.2 Hz, 2H, 2 aromatic H), 6.39 (t, J = 2.2 Hz, 1H, aromatic H), 6.16 (dq, J = 1.8, 1.0 Hz, 1H, HHC=C), 5.59 (dq, J = 1.8, 1.0 Hz, 1H, HHC=C), 5.10 (s, 2H, Bn-CH₂), 4.74 (s, 2H, 2 NH), 3.99 (t, J = 6.0 Hz, 4H, 2 CH₂CH₂O), 3.31 (q, J = 6.2 Hz, 4H, 2 CH₂CH₂NH), 2.03-1.89 (m, 7H, 2 CH₂CH₂CH₂, CH₃), 1.44 (s, 18H, 2 C(CH₃)₃). 

$$^{13}$$C NMR (76 MHz, CDCl₃) δ = 167.1 (C(CO)O), 160.0 (2 aromatic C), 156.0 (2 C=O), 138.4 (H₂C=C), 136.1 (aromatic C), 125.9 (H₂C=C), 106.4 (2 aromatic C), 100.9 (aromatic C), 79.2 (2 C(CH₃)₃), 66.2 (Bn-CH₂), 65.8 (2 CH₂CH₂O), 37.9 (2 CH₂CH₂NH), 29.5 (2 CH₂CH₂CH₂), 28.4 (2 C(CH₃)₃), 18.3 (CH₃). HRMS (ESI-TOF): calcd for C₂₇H₄₃N₂O₈ ([M+H]⁺) 523.3014; found 523.3015. Elemental analysis calcd (%) for C₂₇H₄₂N₂O₈: C 62.05, H 8.10, N 5.36, O 24.49; found: C 61.92, H 8.17, N 5.24, O 24.37. Rf: 0.42 (hexane/EtOAc 2:1).

**General procedure for free radical polymerization (FRP):** AIBN solution (0.5 M in DMF) was freshly prepared in advance. According to Table 1, the required amounts of monomer 1c, DMF, AIBN were added into a Schlenk tube equipped with a magnetic stirring bar. After rapid
homogenization, the mixture was thoroughly degassed by several freeze-pump-thaw cycles and then placed in a pre-heated oil bath at 65 °C for a predetermined time (see Table 1). Progress of the polymerization could macroscopically be assessed through the mixture’s increasing viscosity, ultimately leading to a merely oscillating or stalled stirring bar. The polymerization was quenched by rapid cooling with liquid nitrogen and addition of a small amount of CH₂Cl₂. The dissolved polymerization mixture was purified by column filtration through a short pad of silica gel using CH₂Cl₂ as eluent. Freeze-drying of the oily residue from 1,4-dioxane afforded the polymer (PG1) as a colorless foam.

General procedure for controlled radical polymerization (RAFT): AIBN and CDB solutions (0.5 M in DMF) were freshly prepared in advance. According to Table 1, the required amounts of monomer 1c, DMF, AIBN and CDB were added into a Schlenk tube equipped with a magnetic stirring bar. After rapid homogenization, the mixture was thoroughly degassed by several freeze-pump-thaw cycles and then placed in a pre-heated oil bath at 65 °C for a predetermined time (see Table 1). Progress of the polymerization could macroscopically be assessed through both the increasing viscosity and attenuation of the mixture’s color. The polymerization was quenched by rapid cooling with liquid nitrogen and addition of a small amount of CH₂Cl₂. The dissolved polymerization mixture was purified by column filtration through a short pad of silica gel using CH₂Cl₂ as eluent. Freeze-drying of the oily residue from 1,4-dioxane afforded the polymer (PG1) as a pink foam.
**General procedure for dendronizations:** TFA (20 equiv per amine) was slowly added to PGn at -10 °C and the suspension was allowed to warm to room temperature overnight. Excess TFA was removed from the resulting solution by repeated addition of methanol and evaporation to dryness (5×). The solid residue was taken up in water and freeze-dried to yield dePGn as colorless foam. dePGn (1.0 equiv) and DMAP (0.3 equiv per amine) were dissolved in DMF (c\text{polymer} = 0.5 \text{mmol ml}^{-1}) and Et\text{3}N (2.0 equiv per amine) and the mixture was cooled to -10 °C using an ice/salt freezing mixture. Activated ester 1d (3.0 equiv per amine) was added in the cold, the mixture was allowed to reach room temperature. Two further additions of 1d (1.0 equiv per amine each) were performed over the course of five days. The mixture was stirred for a predetermined amount of time (PG2: 4 d; PG3: 12 d) before the polymer was precipitated twice into ice-cooled Et\text{2}O. The polymer was re-dissolved in CH\text{2}Cl\text{2} and subjected to column filtration through a short pad of silica gel using CH\text{2}Cl\text{2} as the eluent. After evaporation of the solvent, freeze-drying of the residue from 1,4-dioxane gave the polymer (PG\text{n}+1) as a colorless foam.
$^1$H NMR spectrum (CDCl$_3$, 300 MHz) of compound 1b:
$^{13}$C NMR spectrum (CDCl$_3$, 76 MHz) of compound 1b:
$^1$H NMR spectrum (CDCl$_3$, 300 MHz) of compound 1c:
$^{13}$C NMR spectrum (CDCl$_3$, 76 MHz) of compound 1c:
$^1$H NMR spectrum (CDCl$_3$, 300 MHz) of PG1:
$^1$H NMR spectrum (CDCl$_3$, 300 MHz) of PG2:
\textsuperscript{1}H NMR spectrum (CDCl\textsubscript{3}, 300 MHz) of \textbf{PG3}:
S3. Supplementary GPC traces

Figure S2. GPC traces of homologous DPs (PG1-3) with a) $P_n \approx 50$, b) $P_n \approx 300$, c) $P_n \approx 1000$, d) $P_n \approx 1500$, e) $P_n \approx 2000$ and f) $P_n \approx 3000$. The respective peak maxima shift towards shorter retention times with increasing generation.
Figure S3. (a) Second heating DSC thermograms for PG1-3, $P_n \approx 50$. (b) Differentiated DSC traces to better visualize the shift and broadening of the glass transition with increasing generation.
Figure S4. Second heating DSC thermograms (a) and differentiated DSC traces (b) for PG1-3, $P_n \approx 1500$. 
Figure S5. Second heating DSC thermograms (a) and differentiated DSC traces (b) for PG1-3, $P_n \approx 3000$. 
Table S2: Numeric summary of the determined $T_g$ values from DSC measurements.

<table>
<thead>
<tr>
<th>$P_n$</th>
<th>PG1</th>
<th>PG2</th>
<th>PG3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$ [°C]</td>
<td>SD [°C]</td>
<td>$T_g$ [°C]</td>
</tr>
<tr>
<td>50</td>
<td>37.7</td>
<td>1.8</td>
<td>62.7</td>
</tr>
<tr>
<td>300</td>
<td>46.8</td>
<td>0.7</td>
<td>65.1</td>
</tr>
<tr>
<td>1000</td>
<td>51.9</td>
<td>1.7</td>
<td>67.8</td>
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<tr>
<td>1500</td>
<td>53.3</td>
<td>0.4</td>
<td>66.8</td>
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<td>2000</td>
<td>53.8</td>
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<tr>
<td>3000</td>
<td>52.9</td>
<td>1.5</td>
<td>67.1</td>
</tr>
</tbody>
</table>

Note that softening effects caused by traces of residual solvent in the samples may lead to considerable fluctuations in the measured $T_g$ values, as evidenced by the ragged, endothermic jumps in the DSC traces of first heating runs around the boiling point of 1,4-dioxane. The aforementioned impact of residual solvent on the measured $T_g$ values holds especially true for the shortest-chained polymers. On this ground, the samples were extensively dried in vacuum at 80 °C before multiple DSC cycles were performed and checked for overlapping of the heating traces as of the second DSC run.
S5. Supplementary information for simulations

Figure S6: Indicative pair-distance distribution for PG1-50 potentially interacting pairs (a) benzene-benzene (π-stacks), (b) donor-acceptor (hydrogen bonds), and (c) boc-boc. Both intra- and intermolecular interactions are determined. The distance is calculated from the backbone toward the periphery of the DP.

Figure S7: Top: Pair correlation function $g(r)$ as function of center-to-center (backbone) distance $r$, for polymers of given stiffness ($\kappa = 1, 5$ and 20 for (a), (b) and (c), respectively), $l_p = 9.1517$ and different number of repeat units $P_n$. At short length scales, the characteristic intermolecular (DP diameter) is 1 in simulation units. Bottom: Respective orientational order parameter $S_2(r)$ is shown in (d), (e) and (f).
S6. Supplementary information for rheological measurements

In table S3 the constants of the WLF fit for the samples of the series PG1-2-3 are reported.

Table S3: Value of the WLF fit for the supramolecular dendronized polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>c₁</th>
<th>c₂ [°C]</th>
<th>T_{ref} [°C]</th>
<th>c₁g</th>
<th>c₂g</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG1-50</td>
<td>8.7</td>
<td>116.3</td>
<td>90</td>
<td>14.6</td>
<td>69.3</td>
</tr>
<tr>
<td>PG1-1500</td>
<td>8.9</td>
<td>87.9</td>
<td>90</td>
<td>15.4</td>
<td>50.3</td>
</tr>
<tr>
<td>PG1-2000</td>
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<td>96.2</td>
<td>90</td>
<td>15.3</td>
<td>59.2</td>
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<tr>
<td>PG1-3000</td>
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<td>86.1</td>
<td>90</td>
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<td>PG2-50</td>
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<td>100</td>
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<td>58.9</td>
</tr>
<tr>
<td>PG2-1500</td>
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<td>100.0</td>
<td>100</td>
<td>14.7</td>
<td>66.8</td>
</tr>
<tr>
<td>PG2-2000</td>
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<td>96.03</td>
<td>100</td>
<td>14.6</td>
<td>66.3</td>
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<tr>
<td>PG2-3000</td>
<td>8.9</td>
<td>89.3</td>
<td>100</td>
<td>13.4</td>
<td>49.9</td>
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<tr>
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<td>90</td>
<td>15.1</td>
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<td>PG3-1500</td>
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<td>90</td>
<td>14.6</td>
<td>68.9</td>
</tr>
</tbody>
</table>

The C₁ parameter in WLF relates to the fractional free volume f at T=T_g: f(T_g)=2.303 C₁g.

Figure S8 below compares the WLF curves for the three DPs series. Figure S9 depicts the relevant values for all investigated DPs. It is evident that no clear correlation between f and P_n exists.
**Figure S8:** Comparison of WLF fit curves of PGs from figures 14a, 14b and 14c.

**Figure S9:** Values of $f(T_g)$ as a function of the degree of polymerization of PGs.
In order to demonstrate the validity of the Time Temperature Superposition principle, we report below the van Gurp-Palmen Plots corresponding to the mastercurves of figure 10 of the main text (figure S10).\textsuperscript{6}

**Figure S10**: Van Gurp-Palmen plots related to the mastercurves of the PG samples. Temperatures as indicated in the corresponding legends.
S7. Supplementary analysis of entanglements

Here we consider the “thick” dendronized polymers and we attempt at a simple, approximate analysis of their entanglement molar mass by ignoring correlations and bonding interactions. Evidently, this analysis is too idealized and does not apply to the experimental system at hand, but it is aimed at assessing the role of thickness on the ability of such systems to entangle topologically in the absence of other interactions. The Kavassalis – Noolandi theory\(^7,8\) can serve as a guide to estimate the probability to form entanglements in DPs. In a nutshell, it states that for flexible polymers in the Gaussian limit, the number of Kuhn segments between entanglements, \(N_e\) is not constant but it increases with the molecular weight of the polymer, approaching a constant value in the limit of infinitely long chains. In such a case, the asymptotic value of \(N_e\) is given by the following equation:

\[
\lim_{N \to \infty} N_e = \left[6 \left( \tilde{N} + 1 \right)/\pi \Phi \right]^2
\]

where \(\Phi\) is the volume fraction of the polymer and \(\tilde{N}\) is the coordination number. Actually, \(\tilde{N}\) is the number of neighbouring segments (excluding tails) around a test volume, that define an entanglement. The geometric parameter \(\tilde{N}\) accounts for lateral constraints to the motion of a polymer chain in the entanglement volume, hence it can be regarded as the number of segments of length \(N_e\) included in the sphere spaced by an entanglements strand. Here, we consider dendronized polymers in the melt state and then we assume \(\Phi = 1\). Provided that dendronized polymers are thick molecules we expect a lower value of \(\tilde{N}\) compared to conventional linear polymers (usually 20). For this reason, a very conservative value of \(\tilde{N}\) for DPs could be 2 (in fact it should be higher), and from equation 1 we obtain:

\[
\lim_{N \to \infty} N_e = \left[6 \left( 2 + 1 \right)/\pi \right]^2 \cong 30
\]
Given that a typical value of the persistence length is 10 nm for PG1-3, we obtain a maximum contour length between entanglements, $l_e = 30 \cdot 10 = 300$ nm (or 600 nm if we consider the respective Kuhn length). The length of the repeating unit of the DPs coincides with the length of the repeating unit of PMMA backbone, which is approximately 0.25 nm. For a degree of polymerization $P_n=1500$ this gives a contour length of the DP of 375 nm. Therefore, from this simple consideration the onset of entanglements should be above $P_n=1500$, likely between 1500 and 3000. This estimation is consistent with the packing length, $p$, analysis. In such a case, if we consider that DPs are in the dense bottlebrush limit, accounting for the dependence of $p$ on molar mass and end-to-end distance and the low-frequency storage modulus (which we consider to be the plateau modulus $G_e$) of, say, PG2-2000 and PG3-2000 (Fig. 12), the data conform to the scaling $G_e \sim p^{-3}$. Hence, the message for the above simple estimations is that the entanglement molar mass of these polymers is extremely large.
S8. References for supplementary information


