Supporting information for

Poly(methyl methacrylate-*block*-vinyl-*m*-triphenylamine): synthesis by RAFT polymerization and melt-state selfassembly

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Molecular characterization



Fig. S1. Representative ¹H NMR spectra of (a) PVmTPA homopolymer (TPA_{5.4}), (b) PMMA homopolymer (MMA₂₀), and (c) PMMA-*b*-PV*m*TPA diblock copolymer (MMA₂₀TPA_{6.3}) in CDCl₃.



Fig. S2. (a) Differential scanning calorimetry (DSC) data for TPA_{5.4} homopolymer (black). The sample was cooled to -85 °C before heating to 200 °C at a rate of 10 °C/min, and the data shown are from the second heating. The T_g was ~120 °C as determined by the midpoint of the inflection (red). (b) Thermogravimetric analysis (TGA) mass loss data (black) and first derivative (red) for TPA_{5.4} homopolymer acquired under N₂ flow with a 10 °C/min heating rate. The 1% and 5% mass loss occurred at 245 °C and 360 °C, respectively.



Fig. S3. SEC (RI-detector, PS standards) data for MMA₂₀ macroinitiator (dashed line, $M_n = 20$ kDa, D = 1.15) and aliquots of MMA₂₀TPA_{6.3} scaled to monomer conversion (solid lines) corresponding to V*m*TPA monomer conversions of 3.8% (blue, D = 1.14), 17% (red, D = 1.14), 24% (green, D = 1.14), 30% (orange, D = 1.13), 33% (purple, D = 1.13), 38% (cyan, D = 1.13), 41% (magenta, D = 1.13), and 44 % (black, D = 1.13). The molecular weight increased with conversion while retaining relatively low Ds, indicative of a controlled radical polymerization.



Fig. S4. SEC (RI-detector, PS standards) data for (a) MMA₂₂ macroinitiator (black, $M_n = 22.4$ kDa, D = 1.11) and six MMA₂₂TPA_y diblock copolymers: MMA₂₂TPA_{6.8} (blue, $M_n = 30.8$ kDa, D = 1.11), MMA₂₂TPA_{7.4} (red, $M_n = 31.1$ kDa, D = 1.11), MMA₂₂TPA_{8.5} (green, $M_n = 31.8$ kDa, D = 1.10), MMA₂₂TPA_{9.0} (orange, $M_n = 32.0$ kDa, D = 1.11), MMA₂₂TPA_{9.6} (purple, $M_n = 32.6$ kDa, D = 1.11), MMA₂₂TPA_{9.9} (cyan, $M_n = 33.1$ kDa, D = 1.11); (b) MMA₂₀ macroinitiator (black, $M_n = 20.0$ kDa, D = 1.15) and three MMA₂₀TPA_y diblock copolymers: MMA₂₀TPA_{7.1} (blue, $M_n = 31.1$ kDa, D = 1.13), MMA₂₀TPA_{7.9} (red, $M_n = 31.4$ kDa, D = 1.12), MMA₂₀TPA_{8.2} (green, $M_n = 31.8$ kDa, D = 1.12); and (c) MMA₁₂ macroinitiator (black, $M_n = 12.0$ kDa, D = 1.03) and MMA₁₂TPA_{3.9} diblock copolymer (red, $M_n = 20.0$ kDa, D = 1.07). All polymers exhibited a clear shift in molecular weight from PMMA macroinitiators to PMMA-*b*-PV*m*TPA diblock copolymers while maintaining relatively low *D*s indicating controlled chain-extension reactions. (d) SEC data for TPA_{5.4} homopolymer ($M_n = 5.4$ kDa, D = 1.29).

Morphological characterization

We did not observe the $\sqrt{4}q^*$ peak in the SAXS data for the HEX polymers, MMA₂₂TPA_{7.4}, MMA₂₂TPA_{6.8}, and MMA₂₀TPA_{6.3}. For all HEX polymers the expected location of the $\sqrt{4}q^*$ coincided with the calculated first form factor minima (q_{m1}), as illustrated for MMA₂₂TPA_{6.8} in Fig. S5.^{1,2}



Fig S5. Azimuthally-integrated APS-SAXS data (solid line) for HEX MMA₂₂TPA_{6.8} and HEX form factor (dashed line) calculated using the cylinder radius R = 71 Å, determined from q^* and polymer volume fraction.^{1, 2} The expected q value (q = 0.054) for missing $\sqrt{4}q^*$ peak is indicated by the vertical dotted line.



Fig. S6. Azimuthally-integrated NSLS-SAXS data for polymers synthesized from the MMA₂₂ macroinitiator with peak ratios indicated by solid arrows. The peak ratios of q^* , $\sqrt{3}q^*$, $\sqrt{7}q^*$, $\sqrt{9}q^*$ for MMA₂₂TPA_{7.4} were suggestive of a hexagonally-packed cylinder (HEX) morphology. The integer peak ratios for MMA₂₂TPA_{8.5}, MMA₂₂TPA_{9.0}, and MMA₂₂TPA_{9.6} were indicative of lamellar (LAM) morphologies. Expected, but not observed, peak locations are indicated by dashed arrows. Data are shifted vertically for clarity.



Fig. S7. Representative TEM micrographs for (a) $MMA_{22}TPA_{7.4}$, HEX, (b) $MMA_{22}TPA_{8.5}$, LAM, (c) $MMA_{22}TPA_{9.0}$, LAM, and (d) $MMA_{22}TPA_{9.6}$, LAM. Samples were stained with RuO₄ vapor to darken the PV*m*TPA domains. Scale bars represent 100 nm.



Fig. S8. (a) Azimuthally-integrated NSLS-SAXS data of $MMA_{20}TPA_{8.2}$ with peaks indexed for LAM morphology. The expected, but not observed, peak at $3q^*$ is indicated by a dashed arrow. (b) A representative TEM micrograph of $MMA_{20}TPA_{8.2}$ supported the LAM morphology assignment. The sample was stained with RuO₄ vapor to selectively darken the PV*m*TPA domains. The scale bar represents 100 nm.

To further elucidate the morphology of MMA₂₀TPA_{7.1}, samples were partially flow aligned at 175 °C and then annealed for 36 h under vacuum using the setup described by Young et al.³ Briefly, samples were loaded into a Teflon mold attached to a flow channel and heated under a load, which forced the molten sample through the channel. After annealing, the sample was cooled to room temperature, small pieces were cut from the flow-aligned sample for SAXS analysis, and the samples were oriented with respect to flow direction (incident X-ray beam parallel [//] or perpendicular $[\bot]$ to the flow direction). The 2-D SAXS patterns in Fig. S9 were indicative of the HPL morphology. For $MMA_{20}TPA_{7,1}\perp$, there were two strong meridional reflections attributed to the (003) reflection and two weaker reflections at the same azimuthal angle attributed to the (006) reflection, which indicated a layered structure. There were also four weaker off-meridional reflections (at $\sim 53^{\circ}$, indicated by arrows) attributed to the (102) reflection. The value for the azimuthal angle of the (102) reflection in relation to the (003) reflection calculated from the lattice parameters a = 29.5 nm and c = 68.3 nm was 53.2° , which agrees well with the experimental data. Additionally, the reflections were consistent with previous reports for 2-D scattering patterns of HPL samples.³⁻⁹ MMA₂₀TPA₇₁// showed slightly non-uniform scattering rings, likely due to the lack of long-range order of the lamellar normals, which is reasonable for channel-flow aligned samples. Both 1-D SAXS patterns show clear peaks at q^* and $2q^*$ with a broad feature between them. These patterns were consistent with previous reports for HPL samples in which the broad features were attributed to a superposition of higher order reflections from the perforations.^{7, 10, 11}



Fig. S9. 2-D and 1-D (azimuthally-integrated) NSLS-SAXS patterns for $MMA_{20}TPA_{7.1}$ samples oriented with incident X-ray beam parallel ($MMA_{20}TPA_{7.1}$ //) and perpendicular ($MMA_{20}TPA_{7.1}$) to the flow direction. 1-D data were shifted vertically for clarity. The two strong reflections and four weak off-meridional reflections at ~53° (indicated by arrows) in the 2-D pattern for $MMA_{20}TPA_{7.1}$ supported a HPL morphology assignment.

SAXS data were acquired after quenching an MMA₂₀TPA_{7.1} sample from 225 °C to confirm the morphology of the quenched sample was representative of the high temperature morphology. The 1-D SAXS data were consistent with the SAXS data acquired *in situ* at 225 °C, and the peak ratios of q^* , $\sqrt{3}q^*$, $\sqrt{4}q^*$, and $\sqrt{7}q^*$ (see Fig. S10) were indicative of a HEX morphology.



Fig. S10. NSLS-SAXS data acquired at room temperature of an $MMA_{20}TPA_{7.1}$ sample quenched from 225 °C with HEX peak ratios indicated by arrows.

After the two temperature cycles described in the main text, 2-D SAXS data were acquired to confirm the thermal reversibility of the HPL-to-HEX transition (*i.e.* the sample returned to HPL upon cooling). The sample was rotated 90° to obtain $MMA_{20}TPA_{7.1}\perp$ after cooling. As shown in Fig. S11, 1-D and 2-D SAXS patterns were similar to those acquired before the heating cycles, indicating the sample returned to the HPL morphology. Comparing UD-SAXS data for pre- (not shown) and post- (Fig. S11) temperature cycle samples, the 2-D reflections and 1-D peaks were more distinct after the two temperature cycles, indicative of better ordering. This improved ordering likely was a result of the OOT, which facilitated chain reorganization upon cooling.



Fig. S11. 2-D and 1-D UD-SAXS (azimuthally-integrated) patterns for the flow-aligned $MMA_{20}TPA_{7.1}$ sample after two temperature cycles oriented with incident X-ray beam parallel ($MMA_{20}TPA_{7.1}$ //) and perpendicular ($MMA_{20}TPA_{7.1}$) to the flow direction. 1-D data were shifted vertically for clarity. The two strong reflections and four weak off-meridional reflections at ~53° (indicated by arrows) in the 2-D pattern for $MMA_{20}TPA_{7.1}$ supported an HPL morphology assignment.

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