

## SUPPORTING INFORMATION:

### *General information:*

Styrene and 2-vinylpyridine were purchased from Sigma-Aldrich and filtered through neutral Aluminum Oxide (Brockmann grade 1). Methyl methacrylate was purchased from Acros and filtered through inhibitor removers (Sigma-Aldrich). Cumyldithiobenzoate (CDB) was synthesized in a manner analogous to the literature [1], using the less harmful benzylbromide instead of benzylchloride as starting material. 4-(3'-trimethylsilylpropargyloxy)styrene was synthesized according to reference 11 of the main text. The block copolymers were purchased from Polymer Source (Dorval, Canada). ATTO dyes were purchased from ATTO-TEC (Siegen, Germany). The block copolymers, ATTO dyes and all other chemicals were used as received. The Gel Permeation Chromatography (GPC) measurements in THF were performed on a setup using a Waters 515 HPLC pump, a Jasco AS-2055 Plus autosampler, a precolumn and three main columns (PSS SDV, 8 x 300 mm, 5  $\mu$  1000 Å; PSS SDV, 8 x 300 mm, 5  $\mu$ , 10000 Å; PSS SDV, 8 x 300 mm, 5  $\mu$ , 1000000 Å) heated in a column heater at 35 °C with a flow of 1 mL/min. A Ve 3210 UV/Vis detector, a Shimadzu RF-10AXL fluorescence detector and a Waters 4210 RI – detector were used for detection. For measurements with DMac as eluent, a Waters-SEC-system (Consisting of a degasser, 515 pump, column heater, and a DRI 2410 detector) with a Rheodyne injector 772i, a precolumn and three main columns (PSS GRAM, 8 x 50 mm, 10  $\mu$ m; PSS GRAM, 8 x 300 mm, 5  $\mu$ m, 100 Å; PSS GRAM, 8 x 300 mm, 10  $\mu$ m, 1000 Å; PSS GRAM, 8 x 300 mm, 10  $\mu$ m, 3000 Å) was used with a flow of 0.8 mL/ min. All GPC measurements were measured against polystyrene standards. UV/Vis measurements were performed on a CARY 4000. NMR measurements were performed either on a Varian Unity 300 or a Varian Mercury 300.

### *Synthesis of P2VP-SH and dye coupling via thiol-ene reaction:*

Dithiobenzoate-terminated P2VP was synthesized via RAFT-polymerization of 2-vinylpyridine (39 wt% in toluene) in the presence of CDB ( $c_{\text{CDB}} = 5.5 \cdot 10^{-5} \text{ mol} \cdot \text{g}^{-1}$ ) and azobisisobutyronitrile (AIBN,  $c_{\text{AIBN}} = 2.5 \cdot 10^{-5} \text{ mol} \cdot \text{g}^{-1}$ ) for 24 hours. The polymer was precipitated in diethylether, cleaned by dissolution in methanol and re-precipitated in diethylether. Characterization was performed via NMR spectroscopy and Gel Permeation Chromatography (GPC) using DMac as a solvent against polystyrene standards ( $\overline{M}_n = 7000 \text{ g} \cdot \text{mol}^{-1}$ , PDI = 1.2).

The dithiobenzoate-terminated P2VP (1. eq.) and a few crystals of tris(2-carboxyethyl)phosphine hydrochloride (TCEP) were dissolved in dimethyl sulfoxide (DMSO, 2 mL). The mixture was flushed with Argon for 10 minutes. *n*-Butylamine (0.1 mL) was added under an Argon counter-flow and the mixture flushed again for 20 minutes. Glacial acetic acid (0.2 mL) was then added, followed by Maleimide-functionalized dye (1. eq., pre-dissolved in DMSO (1 mL)), under an Argon counter-flow. The mixture was stirred on a shaker for 96 hours. The polymer was precipitated in diethylether (100 mL), washed twice with diethylether (25 mL), twice with water (25 mL), dissolved in methanol and re-precipitated in diethylether. It was washed a final time

with diethylether and dried in vacuum. Via UV/Vis spectroscopy, the dye loading of thiol groups was determined to be 58%.

*Synthesis of PMMA–SH and dye coupling via thiol-ene reaction:*

Dithiobenzoate-terminated PMMA was synthesized by RAFT polymerization of methyl methacrylate (37 wt% in toluene) in the presence of CDB and AIBN ( $c_{\text{AIBN}} = 3.1 \cdot 10^{-5} \text{ mol} \cdot \text{g}^{-1}$ ,  $c_{\text{CDB}} = 1.26 \cdot 10^{-5} \text{ mol} \cdot \text{g}^{-1}$ ) for 24 hours. The polymer was precipitated and washed twice using n-hexane. Characterization was performed via GPC analysis against poly(methyl methacrylate) standards ( $\overline{M}_n = 11850 \text{ g} \cdot \text{mol}^{-1}$ , PDI = 1.28).

The dithiobenzoate-terminated PMMA (1 eq.) and a few crystals of TCEP were dissolved in tetrahydrofuran (THF, 2 mL). The mixture was flushed with Argon for 10 minutes. *n*-Butylamine (0.1 mL) was added in an Argon counter-flow and flushed again with Argon for 20 minutes. This was followed by the introduction of Glacial acetic acid (0.2 mL). Maleimide-functionalized dye (1 eq.) was pre-dissolved in THF (1 mL) and added in an Argon counter-flow. The mixture was stirred on a shaker for 120 hours. The polymer was precipitated in n-hexane (100 mL), washed twice in n-hexane (25 mL) and then twice with water (25 mL). The dye loading of thiol groups was determined to be 71% via UV/Vis spectroscopy. The molecular weight was measured by GPC ( $\overline{M}_n = 13500 \text{ g} \cdot \text{mol}^{-1}$ ).

*Synthesis of statistical poly(2-vinylpyridine-co-4-(3'-trimethylsilylpropargyloxy)styrene):*

AIBN (5.2 mg,  $3.2 \cdot 10^{-5} \text{ mol}$ ) and CDB (42.2 mg,  $1.56 \cdot 10^{-4} \text{ mol}$ ) were dissolved in a solution of 2VP (38.6 wt%) and 2 wt.% 4-(3'-trimethylsilylpropargyloxy)styrene in toluene (2.99 g). The solution was degassed in three pump–freeze–thaw cycles and transferred via a glovebox under an Argon atmosphere into a sample flask. The mixture was heated to 60 °C for 24 hours. The polymer was precipitated into n-hexane (100 mL), washed several times with n-hexane (25 mL) and then dissolved in acetone. Upon solvent evaporation and drying in a vacuum at 40 °C, a red polymer was obtained (0.706 g,  $\overline{M}_n = 8054 \text{ gm} \cdot \text{mol}^{-1}$ ). On average 1.54 Alkyne groups were found per chain by NMR.

*Synthesis of statistical poly(styrene-co-4-(3'-trimethylsilylpropargyloxy)styrene):*

AIBN (29 mg, 0.2 mmol) and CDB (85.8 mg, 0.3 mmol) were dissolved in a solution of 4.5 wt.% 4-(3'-trimethylsilylpropargyloxy)styrene in styrene (5.12 g). The solution was degassed in three pump–freeze–thaw cycles and transferred via a glovebox under an Argon atmosphere into a sample flask. The mixture was heated to 60 °C for 48 hours and precipitated into methanol (100 mL). The polymer was filtered and dried in a vacuum at 40 °C. A red polymer was obtained (2.85 g,  $\overline{M}_n = 9000 \text{ g} \cdot \text{mol}^{-1}$ ). On average 0.84 Alkyne groups were found per chain by NMR.

*Aminolysis and deprotection of the alkyne functional group:*

Polymer (100 mg) and a few crystals of TCEP were dissolved in THF and degassed for 10 minutes with nitrogen. Butyl amine (0.1 mL) was added under a nitrogen counter-flow and

degassed for a further 15 minutes during which time the solution lost its red color. Methyl acrylate (0.2 mL) was added in nitrogen counter-flow and shaken for 20 hours. The polymer was precipitated in n-hexane (50 mL), filtered off and dissolved in acetone. The solvent was removed and the sample dried in vacuum. The sample was then dissolved in THF (1 mL) followed by the addition of tetra-*n*-butyl-ammonium fluoride in THF (0.1 mL, 1 M). This mixture was shaken for 30 minutes. The polymer was then precipitated into water (10 mL), filtered off and dried in vacuum. The conversion of the alkyne function was monitored by NMR spectroscopy. The signal of the TMS-group at 0.12-0.18 ppm was gone after 30 minutes.

*Dye coupling via thermal alkyne-azide cycloaddition for poly-2-vinylpyridine:*

Poly-(2-vinylpyridine-*co*-4-propargyloxystyrene) (5.6 mg) was dissolved in dimethylformamide (DMF). Azide functionalized ATTO-647N (1 mg) was dissolved in DMF and added. The mixture was degassed for 10 minutes with argon and heated at 80 °C for 20 hours. The solvent was then evaporated. The residue was washed with water, dissolved in THF and dried to yield a polymer film. The film was washed with water (10 mL) until the water phase stayed colorless even upon several hours of shaking. The conversion of the alkyne functional groups was determined to be 9% via UV-Vis spectroscopy.

*Dye coupling via thermal alkyne-azide cycloaddition for polystyrene:*

Poly(styrene-*co*-4-propargyloxystyrene) (5.5 mg) was dissolved in DMF. Azide functionalized ATTO-647N (1 mg) was dissolved in DMF and added. The mixture was degassed for 10 minutes with argon and heated at 80 °C for 48 hours. The solvent was evaporated and the residue was washed with water. The residue was dissolved in THF and the solvent was evaporated to form a polymer film. It was washed with water (10 mL) until the water phase stayed colorless after several hours of shaking. Via UV/Vis spectroscopy, a conversion of the alkyne functions of 26 % was determined. The  $\overline{M}_n$  value was measured by GPC to be 9320 g·mol<sup>-1</sup>.

*Fluorescence nanoscopy:*

Imaging of optical xz-cross-sections within bulk polymer was performed with an isoSTED nanoscope similar to the setup described in Ref. 5 of the main text. Briefly, the fluorescent dye A647N was excited at a wavelength of 635 nm by a pulsed semiconductor laser (PDL 800-B with LDH-P-C 635b, PicoQuant, Berlin, Germany) delivering < 100 ps excitation pulses. These were synchronized to STED pulses of ~1 ns length from a frequency doubled fiber laser (ELP-5-775-DG, IPG Photonics Corporation, Oxford, MA) operating at 20 MHz and at a wavelength of 775 nm. In order to optimize contrast, the point spread function was adapted to the lamellar structure of the samples by choosing an oblate shape configuration as described in Ref. 6 of the main text. Detection of the emission was carried out over the 660–700 nm wavelength band using a photon-counting avalanche photodiode (APD) (PerkinElmer, Waltham, MA).

SUPPORTING INFORMATION REFERENCES:

[1] Perrier, S.; Barner-Kowollik, C.; Quinn, J. F.; Vana, P. & Davis, T. P. Origin of Inhibition Effects in the Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization of Methyl Acrylate Macromolecules, 2002, 35, 8300-8306.

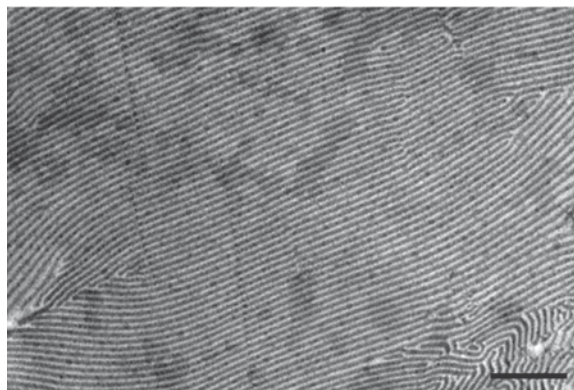


Fig. S1. Transmission Electron Micrograph of PS-PMMA confirming the expected lamellar morphology. Scale bar: 1 $\mu$ m. A Transmission Electron Micrograph confirming the lamellar morphology of the PS-P2VP can be found in Figure 1c of Reference 6 of the main text.

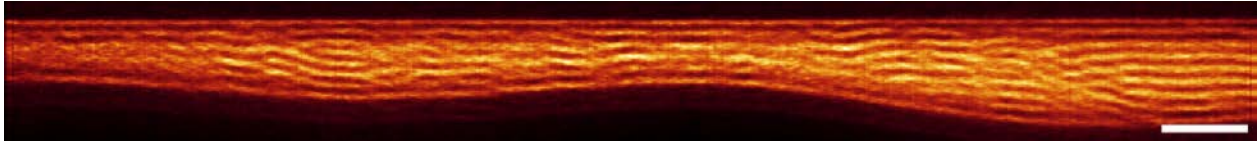


Fig S2. Cross sectional iso-STED image of PS-P2VP. Phase separation was induced by thermal annealing at 170°C for 3 days.