Microphase Separation of High χ , Low *N* Polymers by Photoinduced Copper-Mediated Polymerization, Achieving Sub-2 nm Domains at Half-Pitch

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The lower limit of domain size resolution using microphase separation of short poly(acrylic acid) homopolymers equipped with a short fluorinated tail, posing as an antagonist 'A block' in pseudo AB block copolymers has been investigated. An alkyl halide initiator with a fluorocarbon chain was utilized as a first 'A block' in the synthesis of low molecular weight polymers (1400-4300 g mol⁻¹) using photoinduced Cu(II)-mediated polymerization allowing for very narrow dispersity. Poly(*tert*-butyl acrylate) was synthesized and subsequently deprotected to give very low degrees of polymerization (*N*), amphiphilic polymers with low dispersity ($\mathcal{D} = 1.06-1.13$). By exploiting the high driving force for demixing and the well-defined 'block' sizes, we are able to control the nanostructure in terms of domain size (down to 3.4 nm full-pitch) and morphology. This work demonstrates the simple and highly controlled synthesis of polymers to push the boundaries of the smallest achievable domain sizes obtained from polymer self-assembly.

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Table of Contents

3
4
4
4
4
4
5
14
14

Experimental

Synthesis of perfluorooctyl bromoisobutyrate initiator (PFOBiB)

Procedure adapted from literature.¹ DCM (60 ml), triethylamine (6.46 x 10^{-2} mol, 6.54 g) and 1H,1H,2H,2H, perfluorooctanol (5.36 x 10^{-2} mol, 19.52 g) were added to a 250 ml 3-necked round bottom flask (RBF) equipped with a constant pressure drop funnel. The RBF was purged with nitrogen and cooled in an ice-water bath containing NaCl and acetone. DCM (10 ml) containing α -bromoisobutyryl bromide (8.06 x 10^{-2} mol, 18.53 g) was placed in the constant pressure drop funnel and added dropwise to the reaction flask. The reaction was kept for 2 hrs in the ice-water bath followed by 36 hrs at 25 °C. The resulting solution was extracted (x4) in saturated aqueous NaHCO₃ solution and 1M NaOH solution, drying over anhydrous magnesium sulfate and filtering. Rotary evaporation of the solution resulted in a yellow liquid, which was further purified by flash column chromatography using DCM as the mobile phase and basic alumina as the stationary phase, followed by solvent evaporation under reduced pressure. The resulting yellow liquid was dried in a vacuum oven at 25 °C overnight. Yield 78.4%. ¹H NMR (500 MHz, [D₁]CDCl₃): $\overline{\delta}$ =4.49 (t, ³J_{H,H}=6 Hz, 2H; CO₂CH₂), 2.53 (tt, ³J_{H,H}=6, 18 Hz, 2H; CF₂CH₂), 1.94 ppm (s, 6H; C(CH₃)₂); ¹³C NMR (125.8 MHz, CDCl₃): $\overline{\delta}$ =171.5 (s; CO), 117.6 (tt, ¹J_{C,F}=256, ²J_{C,F}=32 Hz; CF₂CH₂), 117.4 (qt, ¹J_{C,F}=288, ²J_{C,F}=33 Hz; CF₃), 113.7-105.7 (m; (CF₂)₄), 58.0 (t, ³J_{C,F}=4 Hz; CH₂O), 55.1 (s; CBr), 30.7 (s; C(CH₃)₂); 30.5 ppm (t, ²J_{C,F}=22 Hz; CF₂CH₂); ¹⁹F NMR (376.5 MHz, CDCl₃): -81.2 (t, ³J_{C,F}=10 Hz, 3F; CF₃), -113.6--113.9 (m, 2F; CF₃CF₂), -121.9--122.3 (m, 2F; CF₃(CF₂)₄CF₂).

General procedure for photo-induced polymerization - example target F₁₃-Pt-BA₂₅

CuBr₂ (0.02 eq., 2.5 mg) was dissolved in IPA (2 ml) by sonication, followed by addition of Me₆Tren (0.12 eq., 17.6 µl) and *t*-BA (25 eq., 2 ml). The mixture was degassed with nitrogen for 10 min before adding PFOBiB initiator (1 eq., 159 µl) and further degassed for 5 min. The reaction was then left under an ultraviolet lamp (4 x 9W bulbs) for 12 hours. The resulting polymer was dissolved in minimum acetone, precipitated in deionised H₂O and passed through neutral alumina to remove remaining copper. Solvent was removed and product dried in a vacuum oven at 25 °C overnight. ¹H NMR (300 MHz, [D₁]CDCl₃): δ =4.40-4.30 (m 2H; CO₂CH₂), 2.39-1.51 (m, 2H; CF₂CH₂), 1.94 ppm (s, 6H; C(CH₃)₂), 2.39-1.51 (m; (CH₂CH)_n), 1.45 (s; ((CH₃)₃)_n), 1.23 (s, 2H; COCH₂CH₂), 1.15 ppm (s, 6H; (CH₃)₂). 99% conversion obtained by ¹H NMR. $\mathcal{D}_{GPC(THF)}$ = 1.13, M_{n,GPC} = 4300 g mol⁻¹.

Deprotection of Pt-BA – example target F₁₃-PAA₂₅

100 mg of F_{13} -Pt-BA₂₅ was dissolved in 1 ml DCM. 1 ml TFA was added and stirred at room temperature overnight. TFA was removed using a rotary evaporator and residual TFA was removed with the addition of acetone to form an azeotrope (x3). The product was then dissolved in EtOH and precipitated in hexane, solvent removed and subsequently dried under vacuum at 25°C overnight. ¹H NMR (400 MHz, [D₁]CDCl₃): δ =4.52-4.47 (m, 1H; CHBr), 4.40-4.28 (m, 2H; CO₂CH₂), 2.75-1.41 (m; ((CH₃)₃)_n), 1.32 (s, 2H; COCH₂CH₂), 1.20 (d, 6H; (CH₃)₂). 99% conversion obtained by ¹H NMR. M_{n,MALDI} = 2097 g mol⁻¹.

Instrumentation

We are grateful for the Polymer Characterisation RTP for providing use of the following equipment: Agilent Infinity II MDS GPC-SEC instruments with DMF and THF eluents. We are also grateful to the University of Warwick department of Chemistry for the use of a Bruker autoflex for MALDI-ToF-MS and the Department of Physics for use of Xenocs Xeuss 2.0 for SAXS.

¹H NMR. NMR spectra were recorded on Bruker HD-300 MHz, HD-400 MHz spectrometers and a Bruker AV III-500 MHz HD spectrometer using a cryoprobe. Monomer conversion was calculated by comparison of vinyl protons (6.4-5.6 ppm) with $(CH_3)_3$ protons (1.45 ppm) of Pt-BA.

Size Exclusion Chromatography

THF - **Standard.** Agilent Infinity II MDS instrument equipped with differential refractive index (DRI), viscometry (VS), dual angle light scatter (LS) and multiple wavelength UV detectors. The system was equipped with 2 x PLgel Mixed C columns (300 x 7.5 mm) and a PLgel 5 μ m guard column. The eluent is THF with 2 % TEA (triethylamine) and 0.01 % BHT (butylated hydroxytoluene) additives. Samples were run at 1ml/min at 30'C. Poly(methyl methacrylate) and polystyrene standards (Agilent EasyVials) were used for calibration. Analyte samples were filtered through a GVHP membrane with 0.22 μ m pore size before injection. Respectively, experimental molar mass ($M_{n,SEC}$) and dispersity (\mathcal{D}) values of synthesized polymers were determined by conventional calibration using Agilent GPC/SEC software.

THF - **OligoPore**. Agilent Infinity II MDS instrument equipped with differential refractive index (DRI) and a 220 nm wavelength UV detector. The system was equipped with an OligoPore column (300 x 7.5 mm) and a PLgel 5 μ m guard column. The eluent is THF with no additives. Samples were run at 1ml/min at 30'C. Methyl methacrylate oligomers were used for calibration. Analyte samples were filtered through a GVHP membrane with 0.22 μ m pore size before injection. Respectively, experimental molar mass ($M_{n,SEC}$) and dispersity (\mathcal{D}) values of synthesized polymers were determined by conventional calibration using Agilent GPC/SEC software.

MALDI-ToF-MS

Samples for MALDI ToF analysis were dissolved at 10 mg/ml in THF with 1 mg/ml of sodium iodide. 10 µl of this sample mixture was then mixed with 10 µl matrix solution of 40 mg/ml trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) in THF and 1mg/ml of sodium iodide. 0.5 µl of the resulting solution was then spotted on a 384 ground steel multi target plate, using a dried droplet methodology. The dried crystal structure was then analysed using a Bruker autoflex, equipped with a 337 nm N2 laser, operating in reflectron positive mode with an ion source voltage of 19 kV. Data analysis was then carried out on Bruker fleXanalysis and mMass.

Small-Angle X-Ray Scattering

Small-angle X-ray scattering (SAXS) measurements were made using a Xenocs Xeuss 2.0 equipped with a micro-focus Cu Ka source collimated with Scatterless slits. The scattering was measured using a Pilatus 300k detector with a pixel size of 0.172 mm x 0.172 mm. The detector was translated vertically and the images combined to form a virtual detector with double the number of pixels. The distance between the detector and the sample was calibrated using silver behenate (AgC₂₂H₄₃O₂), giving a value of 0.339(5) m. The magnitude of the scattering vector (*q*) is given by $q=4\pi\sin\theta/\lambda$, where 2 θ is the angle between the incident and scattered X-rays and λ is the wavelength of the incident X-rays. This gave a q range for the detector of 0.035 Å⁻¹ to 1.66 Å⁻¹. A Pilatus 100k was also used to measure the wider-angle scattering response. This detector was static at an angle of 36° to the beam direction and at a distance of 0.162(2) m. Giving a q range for the detector of to 1.31 Å⁻¹ to 3.27 Å⁻¹. The samples were mounted between two sticky Kapton windows. A radial integration as function of q was performed on the 2D scattering profile and the resulting data corrected for the absorption and background from the sample holder. The wider-angle data were rescaled to match the scale of the SAXS measurements.

Transmission Electron Microscopy

TEM micrographs were obtained using a JEOL JEM-2100 transmission electron microscope at an accelerating voltage of 200 kV. The samples for TEM were prepared by dropcasting 7 μ L of the diluted solution (1-3 mg of sample dissolved in 1 mL of methanol) onto graphene oxide-copper grids supplied by EM Resolutions and were left to dry at room temperature for 30 minutes. For the solvent annealing, the dropcasted grids were placed under a MeOH-rich environment for 24 hours. For the thermal annealing, the dropcasted grids were first left to dry at ambient temperature and then placed in an oven for 24 hours at 120 degrees.

Differential Scanning Calorimetry

Mettler-Toledo DSC1 instrument with autosampler. Samples were cooled with liquid nitrogen and heated at a rate of 10 °C/min from -30 to 180 °C.

Results and Discussion



Figure S1. ¹H NMR of perfluorooctyl bromoisobutyrate initiator (PFOBiB) in CDCl₃.



Figure S2. ¹³C NMR of perfluorooctyl bromoisobutyrate initiator (PFOBiB) in CDCI₃.



Figure S3. ¹⁹F NMR of perfluorooctyl bromoisobutyrate initiator (PFOBiB) in CDCl₃.

Table S1. Initiator efficacy characteristi	cs for PFOBiB.
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Reaction	M _{n, NMR} (g mol ⁻¹)	Conversion (%)	End Group Fidelity (%)	Dispersity
PFOBiB, DMSO, methyl acrylate	5400	99	94	1.19
PFOBiB, DMSO, methyl acrylate	27400	>99	58*	1.15
PFOBiB, DMSO, methyl acrylate	54100	99	15*	1.32

*note – intensity of the single terminal backbone proton is lost to noise with increasing molecular weight.



Figure S4. GPC-SEC traces F₁₃-Pt-BA_n. Numbers indicate total degree of polymerization (*N*), including the short fluorinated 'block'.



Figure S5. ¹H NMR comparison of F_{13} -PAA₁₁ and F_{13} -Pt-BA₁₁.



 $\label{eq:Figure S6.} \ensuremath{\mathsf{Figure S6.}} \ensuremath{\mathsf{Key}} \ensuremath{\mathsf{of}} \ensuremath{\mathsf{various}} \ensuremath{\mathsf{end}} \ensuremath{\mathsf{groups}} \ensuremath{\mathsf{observed}} \ensuremath{\mathsf{in}} \ensuremath{\mathsf{MALDI}} \ensuremath{\mathsf{spectra}} \ensuremath{\mathsf{in}} \ensuremath{\mathsf{MALDI}} \ensuremath{\mathsf{spectra}} \ensuremath{\mathsf{in}} \ensuremath{in} \ensuremath{\mathsf{in}} \ensuremath{\mathsf{in}} \ensuremath{\mathsf{in}} \ensuremath{\mathsf{in}} \ensuremath{\mathsf{in}} \ensuremath{\mathsf{in}} \ensuremath{\mathsf{in}} \ensuremath{\mathsf{in}} \ensuremath{in} \ensuremath{\mathsf{in}} \ensuremath{\mathsf{in}} \ensuremath{\mathsf{in}} \ensuremath{in} \ensuremath{\mathsf{in}} \ensuremath{in} \ensur$



Figure S7. MALDI-ToF-MS spectrum of F_{13} -PAA₄. Key of end groups in S7.





Figure S8. MALDI-ToF-MS spectrum of F_{13} -PAA₆. Key of end groups in S7.

Intensity / A.U. Intensity / A.U. m/z m/z Intensity / A.U. m/z m/z

Figure S9. MALDI-ToF-MS spectrum of F_{13} -PAA₉. Key of end groups in S7.

Figure S10. MALDI-ToF-MS spectrum of $\mathsf{F}_{13}\text{-}\mathsf{PAA}_{11}.$ Key of end groups in S7.



Figure S11. MALDI-ToF-MS spectrum of F_{13} -PAA₁₈. Key of end groups in S7.



Figure S12. MALDI-ToF-MS spectrum of F_{13} -PAA₂₅. Key of end groups in S7.



Figure S13. a) DSC traces for F_{13} -PAA_n polymers where N = 11-35. b) Plot of glass transition temperature versus total degree of polymerisation.



Figure S14. SAXS profile of perfluorooctyl bromoisobutyrate initiator (PFOBiB). Note – artifacts arise when integrating from 2D to 1D due to the gaps between detectors.



Figure S15. SAXS/WAXS profiles for EBiB-PAA_n polymer films where n = 5, 10 & 15, prepared by thermal annealing (TA).



Figure S16. SAXS/WAXS profile for thermally annealed F13-PAAn films. Numbers indicate the total degree of polymerization, N.

S17. Calculation of volume fraction of F13-PAAn.



Figure S17. Chemical structure of the block copolymers in this work, where the colours indicate the chemical groups attributed to the separate blocks (fluorinated block in red and PAA block in blue).

The volume fractions of each block were calculated to account for the bridging unit between the 'polytetrafluoroethene' (PTFE) and PAA blocks. The degree of polymerisation (DP) of the fluorinated block was counted as 3 in all polymers (*i.e.* three tetrafluoroethylene, TFE, repeat units). An additional unit was added to the DP of the PTFE block in the volume fraction calculations to account for the adjacent ethylene unit which is approximated to have the same volume as a TFE repeat unit, taking the DP of the PTFE unit to 4. The DP of the PAA blocks differed in each polymer. When calculating the volume fractions of this block an additional repeat unit was added to account for the adjacent ester unit and approximated to have the same volume as the AA units. Figure S17 shows how the polymer was compartmentalised for the volume fraction calculations. The PTFE block with its adjacent ethylene unit is shown in red and the PAA block with the neighbouring ester unit in blue.

The volume fractions were calculated using the following equations:

$$f_{PAA} = \frac{(N_{PAA} \times Mr_{AA})/\rho_{PAA}}{\binom{(N_{PAA} \times Mr_{AA})}{\rho_{PAA}} + \binom{(N_{PTFE} \times Mr_{TFE})}{\rho_{PTFE}}} \qquad f_{PTFE} = 1 - f_{PAA}$$

where N_{PAA} and N_{PTFE} are the degrees of polymerisation of the PAA and PTFE blocks, respectively, each with an additional unit added to account for the bridging unit. $M_{r,AA}$ is the molar mass of acrylic acid (72.06 g mol⁻¹) and $M_{r,TFE}$ is the molar mass of tetrafluoroethene (100.02 g/mol). ρ_{PAA} and ρ_{PTFE} are the densities of PAA and PTFE which are taken as 1.41 and 2.2 g/mL, respectively.

Sample	N _{PAA}	N _{PTFE}	N _{total}	f _{PAA}	f _{PTFE}
F ₁₃ -PAA ₄	5	4	9	0.58	0.42
F ₁₃ -PAA ₅	6	4	10	0.63	0.37
F ₁₃ -PAA ₆	7	4	11	0.66	0.34
F ₁₃ -PAA ₉	10	4	14	0.74	0.26
F ₁₃ -PAA ₁₁	12	4	16	0.77	0.23
F ₁₃ -PAA ₁₅	16	4	20	0.82	0.18
F ₁₃ -PAA ₁₈	19	4	23	0.84	0.16

Table S2. DP values and calculated volume fractions used for each block copolymer in this work.



Figure S18. TEM image of thermally annealed a) F_{13} -PAA₆ b) F_{13} -PAA₆ zoomed c) F_{13} -PAA₁₈.

References

1 L.-W. Zhu, B.-H. Wu, L.-S. Wan and Z.-K. Xu, *Polym. Chem.*, 2014, **5**, 4311–4320.

Author Contributions

E.H. - conducted synthesis of all polymers, materials and the vast majority of characterization. Also designed experiments.

- E.L. conducted TEM and general advice/input.
- G. R. J. initial input, advice and experiment design.
- J. S. T. conducted MALDI-ToF-MS and analysis.
- S. A. L. preliminary data handling and volume fraction calculation.
- S. H. conducted SAXS and interpretation.
- M. J. G. modelling knowledge of block copolymer assemblies.

P. D. T – knowledge and input of SAXS interpretation and block copolymer self-assembly.

D. M. H. – primary supervisor.