

Supporting Info

Materials. Styrene (Acros Organics, 99%) and *tert*-butyl acrylate (*t*BA, Acros Organics, 99%) were dried overnight over CaH₂ and distilled under reduced pressure. *N*-isopropylacrylamide (NIPAM, TCI, >98%) was recrystallized twice from hexane prior to use. 2,2'-Azobis(2-methylpropionitrile) (AIBN, Fluka, 98+%) was recrystallized twice from methanol. Copper(I) bromide (Sigma-Aldrich, 98%) was stirred for 1h in glacial acetic acid and then filtered and washed with acetic acid and ethanol before drying under vacuum. The RAFT agents 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid 3-azido-1-propanol ester (CTA-azide) and 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid propargyl ester (CTA-alkyne) were prepared according to literature procedures.^{1,2} Vinylidene fluoride (VDF, Synquest Labs, 98%), Oxalyl chloride (Acros, 98%), 4-(chloromethyl)benzoic acid (TCI, 98%), 4-((trimethylsilyl) ethynyl) benzoic acid (Sigma-Aldrich), lithium peroxide (Li₂O₂, Acros, 95%), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, Acros, 99+%), 1-dodecanethiol (TCI, >95.0%), tricaprylmethylammonium chloride (Aliquat 336, TCI), carbon disulfide (Acros Organics, 99.9%), sodium hydroxide (Acros Organics, 98%), hydrochloric acid (Boom, 37%), propargyl alcohol (Acros Organics, 99%), 3-bromo-1-propanol (Acros, 97%), *N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDCI-HCL, TCI, >98%), 4-(dimethylamino)pyridine (Sigma-Aldrich, >99%), sodium azide (Sigma-Aldrich, >99.5%), *N,N*-dimethylformamide (DMF, Acros Organics, anhydrous, 99.8%), dichloromethane (DCM, Acros Organics, ≥99.8%) were used as received. All other solvents were analytical grade.

Synthesis of 4-(chloromethyl)benzoyl peroxide. To a stirred solution of 4-(chloromethyl)benzoic acid (5 g, 29.5 mmol) in 25 mL of anhydrous DCM, oxalyl chloride (2.7 mL, 31.5 mmol) and few drops of anhydrous DMF were added at 0 °C. The reaction mixture was left to stir for 2 h at room temperature, after which the solvent was removed *in vacuo*. The remaining residue was dissolved in a mixture of *n*-hexane: Et₂O (50 mL 1:1) and slowly added to a vigorously stirred water solution of Li₂O₂ (1.75 g, 37.5 mmol in 25 mL) at 0 °C. After 3 h, the reaction mixture was diluted with chloroform and extracted twice with water. Subsequently, the aqueous phase was extracted two times with chloroform. The combined organic phases were dried over MgSO₄ and the solvent was removed *in vacuo*. Recrystallization from chloroform yielded white needle-shaped crystals. ¹H-NMR (400 MHz, CDCl₃): δ= 8.07 (d, 4H, -ArH), 7.56 (d, 4H, -ArH), 4.64 (s, 4H, -PhCH₂Cl)

Synthesis of 4-((trimethylsilyl)ethynyl)benzoyl peroxide. To a slurry of 4-((trimethylsilyl) ethynyl) benzoic acid (5 g, 23 mmol) in 25 mL of anhydrous DCM, oxalyl chloride (2.2 mL, 25 mmol) and few drops of anhydrous DMF were added at 0 °C. The reaction mixture was left to stir for 2.5 h at room temperature, after which the solvent was removed *in vacuo*. The remaining residue was dissolved in a mixture of *n*-hexane:Et₂O (50 mL 1:1) and slowly added to a vigorously stirred water solution of Li₂O₂ (1.75 g, 37.5 mmol in 25 mL) at 0 °C. After 3 h, the reaction mixture was diluted with chloroform and extracted twice with water. After this, the aqueous phase was extracted two times with chloroform. The combined organic phases were dried over MgSO₄ and the solvent was removed *in vacuo*. Precipitation from chloroform (20 mL) in methanol (100 mL) yielded a white product. ¹H-NMR (400 MHz, CDCl₃): δ= 7.99 (d, 4H, -ArH), 7.57 (d, 4H, -ArH), 0.27 (s, 18H, -Si-(CH₃)₃)

Synthesis of chlorine-terminated PVDF. A solution of 4-(chloromethyl)benzoyl peroxide (1 g, 3.0 mmol) in 300 mL of anhydrous acetonitrile was introduced into a 600 mL Parr (model 4568) high pressure reactor and purged with N₂ for 30 min. 20 bars of VDF was subsequently transferred in the reactor at room temperature. The temperature inside reactor was increased to 90 °C and the reaction

mixture was stirred at 500 rpm for additional 3 hours. The reactor was cooled down by water to room temperature and depressurized to remove unreacted monomer. The solvent was removed *in vacuo* and the obtained solid was washed multiple times with chloroform to remove the initiator residues. The polymer was finally dried *in vacuo* at 45 °C to obtain a white product. ¹H NMR (400 MHz, acetone-*d*₆): δ = 8.07 (d, -ArH), 7.65 (d, -ArH), 4.80 (s, -PhCH₂Cl), 4.68 (m, -COOCH₂CF₂-), 3.10-2.70 (m, -CF₂CH₂-CF₂CH₂-, head-to-tail), 2.40-2.20 (m, -CF₂CH₂-CH₂CF₂-, tail-to-tail).

Synthesis of azide-terminated PVDF. Chlorine-terminated PVDF (5 g, 0.34 mmol) and NaN₃ (448 mg, 6.89 mmol) were dissolved in 60 mL of DMF and stirred overnight at 60 °C. The polymer solution was concentrated and precipitated three times in MeOH:water (1:1). Subsequent drying of the light-yellow polymer *in vacuo* at 45 °C yielded azide terminated PVDF. ¹H NMR (400 MHz, acetone-*d*₆): δ = 8.07 (d, -ArH), 7.65 (d, -ArH), 4.68 (m, -COOCH₂CF₂-), 4.60 (s, -PhCH₂N₃), 3.10-2.70 (m, -CF₂CH₂-CF₂CH₂-, head-to-tail), 2.40-2.20 (m, -CF₂CH₂-CH₂CF₂-, tail-to-tail).

Synthesis of (TMS-alkyne)-terminated PVDF. A solution of 4-((trimethylsilyl)ethynyl)benzoyl peroxide (1.3 g, 3.0 mmol) in 300 mL of anhydrous acetonitrile was introduced into a 600 mL Parr (model 4568) high pressure reactor and purged with N₂ for 30 min. 20 bars of VDF was subsequently transferred in the reactor at room temperature. The temperature inside reactor was increased to 90 °C and the reaction mixture was stirred at 500 rpm for additional 3 hours. The reactor was cooled down by water to room temperature and depressurized to remove unreacted monomer. The solvent was removed *in vacuo* and the obtained solid was washed multiple times with chloroform to remove the initiator residues. The polymer was finally dried *in vacuo* at room temperature to obtain a light-yellow product. ¹H NMR (400 MHz, acetone-*d*₆): δ = 7.99 (d, ArH), 7.63 (d, ArH), 4.68 (m, -COO-CH₂CF₂-), 3.10-2.70 (m, -CF₂CH₂-CF₂CH₂-, head-to-tail), 2.40-2.20 (m, -CF₂CH₂-CH₂CF₂-, tail-to-tail), 0.22 (s, -Si-(CH₃)₃).

Synthesis of alkyne-terminated PVDF. DBU (49.8 μL, 0.33 mmol) was added to a solution of (TMS-alkyne)-terminated PVDF (2 g, 0.16 mmol) in 200 mL of a mixture of acetonitrile:water (19:1 vol:vol). The reaction mixture was stirred for 2 hours at 60 °C. The solvent was removed *in vacuo* and the polymer was precipitated from DMF in a mixture of MeOH:water (1:1). After filtration the polymer was thoroughly washed with MeOH and DCM and finally dried *in vacuo* at room temperature to yield a light-brown polymer. ¹H NMR (400 MHz, acetone-*d*₆): δ = 8.01 (d, ArH), 7.66 (d, ArH), 4.68 (m, -COO-CH₂CF₂-), 4.51 (s, -CH, alkyne), 3.10-2.70 (m, -CF₂CH₂-CF₂CH₂-, head-to-tail), 2.40-2.20 (m, -CF₂CH₂-CH₂CF₂-, tail-to-tail).

Synthesis of alkyne/azide-terminated PS. A typical procedure of the RAFT polymerization of styrene is as follows. Styrene monomer (9.6 mL, 84 mmol), RAFT agent (CTA-alkyne or CTA-azide) and AIBN in a molar ratio 700:1:0.1 were added to a dried Schlenk tube. The mixture was subjected to at least three freeze-pump-thaw cycles and placed in an oil bath preheated to 70 °C. After reacting for 6 h, the reaction was terminated by cooling in liquid N₂ and the solution was precipitated in a large excess of methanol. The polymer was collected via filtration and reprecipitated two more times from chloroform by methanol. The resulting polymer was dried overnight *in vacuo* at room temperature to remove all traces of residual solvent.

Alkyne-PS

¹H NMR (400 MHz, CDCl₃): δ = 7.40-6.25 (m, C₆H₅), 4.83 (m, -S(C=S)S-CH(Ar)-), 4.09 (m, -COO-CH₂-), 3.27 (-CH₂-S(C=S)S-), 2.71 (s, -CH, alkyne), 2.40-1.20 (m, -CH₂CH(Ar)-), 0.99-0.81 (m, -alkyl)

Azide-PS

^1H NMR (400 MHz, CDCl_3): δ = 7.40-6.25 (m, C_6H_5), 4.83 (m, $-\text{S}(\text{C}=\text{S})\text{S}-\text{CH}(\text{Ar})-$), 4.15 (m, $-\text{COO}-\text{CH}_2-$), 3.27 ($-\text{CH}_2-\text{S}(\text{C}=\text{S})\text{S}-$), 2.40-1.20 (m, $-\text{CH}_2\text{CH}(\text{Ar})-$), 0.99-0.81 (m, -alkyl)

Synthesis of alkyne/azide-terminated PtBA. In a 25 ml Schlenk tube, monomer *t*BA (2 mL, 13.6 mmol), RAFT agent (CTA-alkyne or CTA-azide) and AIBN (at molar ratio 100:1:0.15) were dissolved in 4 mL of anhydrous DMF. After three freeze-pump-thaw cycles, the polymer mixture was placed in an oil bath at 70 °C and stirred for the next 2 h. The reaction was terminated by rapid cooling using liquid N_2 and the polymer was isolated by precipitation three times from DMF into a 20-fold excess of cold MeOH:water (1:1). The obtained yellow powder was dried *in vacuo* at room temperature for 2 days.

Alkyne-PtBA

^1H NMR (400 MHz, CDCl_3): δ = 4.64 (m, $-\text{COO}-\text{CH}_2-$), 3.27 (t, $-\text{CH}_2-\text{S}(\text{C}=\text{S})\text{S}-$), 2.87 (s, $-\text{CH}$, alkyne) 2.20 (m, $-\text{CH}_2\text{CH}(\text{COOtBu})$), 1.80 (m, $-\text{CH}_2\text{CH}(\text{COOtBu})$), 1.40 (m, $-(\text{COOtBu})$), 0.85 (m, -alkyl)

Azide- PtBA

^1H NMR (400 MHz, CDCl_3): δ = 4.20 (m, $-\text{COO}-\text{CH}_2-$), 3.40 (t, $-\text{CH}_2-\text{S}(\text{C}=\text{S})\text{S}-$), 2.20 (m, $-\text{CH}_2\text{CH}(\text{COOtBu})$), 1.80 (m, $-\text{CH}_2\text{CH}(\text{COOtBu})$), 1.40 (m, $-(\text{COOtBu})$), 0.85 (m, -alkyl)

Synthesis of alkyne/azide-terminated PNIPAAm. Anhydrous DMF (4 mL), NIPAAm (1.54 g, 13.6 mmol), RAFT agent (CTA-alkyne or CTA-azide) and AIBN (at molar ratio 100:1:0.15) were introduced into a pre-dried Schlenk tube and subjected to three freeze-pump-thaw cycles. After backfilling the Schlenk tube with nitrogen, the reaction proceeded at 70 °C for 2 h. The reaction mixture was cooled down using liquid N_2 and precipitated three times into diethyl ether. The obtained product was dried for a few hours *in vacuo* at room temperature.

Alkyne-PNIPAAm

^1H NMR (400 MHz, CDCl_3): δ = 6.10 (s, $-\text{NH}-\text{CH}(\text{CH}_3)_2$), 4.65 (m, $-\text{COO}-\text{CH}_2-$), 4.00 (m, $-\text{NH}-\text{CH}(\text{CH}_3)_2$), 3.32 (t, $-\text{CH}_2-\text{S}(\text{C}=\text{S})\text{S}-$), 2.10 (m, $-\text{CH}_2\text{CH}-\text{COO}-$), 1.60 (m, $-\text{CH}_2\text{CH}-\text{COO}-$), 1.13 (m, $-\text{NH}-\text{CH}(\text{CH}_3)_2$), 0.86 (t, -alkyl)

Azide-PNIPAAm

^1H NMR (400 MHz, CDCl_3): δ = 6.10 (s, $-\text{NH}-\text{CH}(\text{CH}_3)_2$), 4.20 (m, $-\text{COO}-\text{CH}_2-$), 4.00 (m, $-\text{NH}-\text{CH}(\text{CH}_3)_2$), 3.32 (t, $-\text{CH}_2-\text{S}(\text{C}=\text{S})\text{S}-$), 2.10 (m, $-\text{CH}_2\text{CH}-\text{COO}-$), 1.60 (m, $-\text{CH}_2\text{CH}-\text{COO}-$), 1.13 (m, $-\text{NH}-\text{CH}(\text{CH}_3)_2$), 0.86 (t, -alkyl)

General procedure for the preparation of PVDF based block copolymers. A general route for the Cu-catalyzed alkyne azide cycloaddition (CuAAC) used for the preparation of block copolymers is described below. The azide/alkyne-terminated PVDF (300 mg, 0.021 mmol for azide-terminated, 0.024 mmol for alkyne-terminated PVDF), the other polymer (PS, PtBA or PNIPAAm) and CuBr were added into dried Schlenk tube in a molar ratio [PVDF]:[polymer]:[CuBr] = 1:2.6:4. After performing a degassing procedure (three repetitive cycles of evacuating and backfilling with N_2), 4 mL of anhydrous DMF was added, followed by PMDETA (30 μL , 0.14 mmol). The reaction was allowed to stir for 3 days at 60 °C and afterwards terminated by exposition to air. The reaction mixture was filtered through a short neutral alumina column in order to remove copper catalyst. The solution was concentrated under reduced pressure and precipitated in a 20-fold excess of nonsolvent (MeOH:water (1:1) for the block copolymers containing PS and PtBA, and cold diethyl ether for the block copolymer with PNIPAAm). After filtration the product was collected via filtration and dried overnight *in vacuo* at room temperature.

Purification of the PVDF based block copolymers. Having in mind that we used excess of the other polymer compared to PVDF end groups, in order to have a complete reaction and to avoid PS, PtBA or PNIPAAm homopolymer contaminations, the residual excess of these polymers had to be removed to get pure block copolymers. The unreacted homopolymers were removed by selective dissolution in a relatively good solvent for them, but nonsolvent for block copolymers (Table S1). Previously dried products were mixed with the selective solvent and subjected to centrifugation (5 min at 4500 rpm). Unreacted homopolymer remained dissolved while the block copolymer separated on the bottom. The procedure was repeated a few times until all homopolymer was removed. The products collected after centrifugation were furthermore dried *in vacuo* at 45 °C in order to get pure block copolymers.

Table S1 Selective solvents used for purification of block copolymers

Block copolymer	Selective solvent
PS- <i>b</i> -PVDF- <i>b</i> -PS	Diethyl ether
PtBA- <i>b</i> -PVDF- <i>b</i> -PtBA	Diethyl ether or methanol
PNIPAAm- <i>b</i> -PVDF- <i>b</i> -PNIPAAm	Water

Characterization.

Nuclear Magnetic Resonance Spectroscopy (¹H NMR) was performed on a 400 MHz Varian (VXR) spectrometer at a room temperature.

Gel Permeation Chromatography (GPC) of PVDF and its block copolymers was performed in DMF (containing 0.01 M LiBr) using a Viscotek GPCmax equipped with a model 302 TDA detectors and two columns (Agilent Technologies-PolarGel-L and M, 8 µm 30 cm) at a flow rate of 1.0 mL min⁻¹ and 50 °C. Prior to the measurements, the block copolymer samples were passed through a alumina column to remove copper catalyst that can induce the aggregation of the block copolymer samples on the column, and filtrated through PTFE filter with 0,20 µm pore size. Narrow dispersity PMMA standards (Polymer Laboratories) were used for constructing the universal calibration curve applied for determining molecular weights. The molecular weight and the polydispersity indices (PDI) of PS, PtBA and PNIPAAm were determined using triple detection method (refractive index, viscosity and light scattering) using THF, stabilized with BHT, as the eluent at a flow rate 1.0 mL min⁻¹ at 35 °C. The separation was carried out by utilizing two PLgel 5 µm MIXED-C, 300 mm columns (Agilent Technologies) calibrated with narrow MWD polystyrene standards (Agilent Technologies and Polymer Laboratories). Predetermined refractive indices (dn/dc) of 0.185, 0.0512 and 0.034 mL g⁻¹ were used for PS, PtBA and PNIPAAm, respectively.

Differential Scanning Calorimetry (DSC) thermograms were recorded on a TA Instruments DSC Q1000 by heating the sample to 200 °C, then equilibrating for 30 min before cooling to room temperature at 10 °C min⁻¹ and then heating again to 200 °C at 10 °C min⁻¹.

Small-angle X-ray scattering (SAXS) measurements were carried out at the Dutch-Belgium Beamline (DUBBLE) station BM26B of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.^{3,4}The sample to detector distance was ca. 3.5 m. The scattering vector q is defined as $q = 4\pi/\lambda(\sin \theta)$ with 2θ being the scattering angle and λ the wavelength of the X-rays (1.03 Å).

Transmission electron microscopy (TEM) was performed on a Philips CM12 transmission electron microscope operating at an accelerating voltage of 120 kV. Prior to imaging, polymer films were obtained via casting of block polymer solutions in DMF into a glass Petri dish. The solvent was allowed to evaporate at 45 °C for two days. Obtained films were thermally annealed at 200 °C for 30 min and

subsequently cooled down to room temperature at $10\text{ }^{\circ}\text{C min}^{-1}$. A piece of the block copolymer film was embedded in epoxy resin (Epofix, Electron Microscopy Sciences) and subsequently microtomed using a Leica Ultracut UCT-ultramicrotome in order to prepare ultrathin sections (ca. 80 nm). No additional staining of the samples was performed.

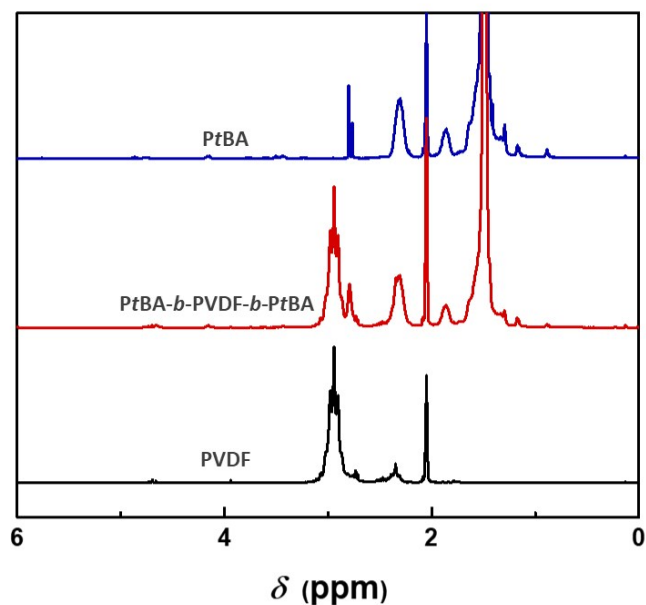


Figure S1 ^1H -NMR spectra ($\text{acetone-}d_6$) of PVDF, PtBA and its block copolymer showing signals of both polymers after click reaction

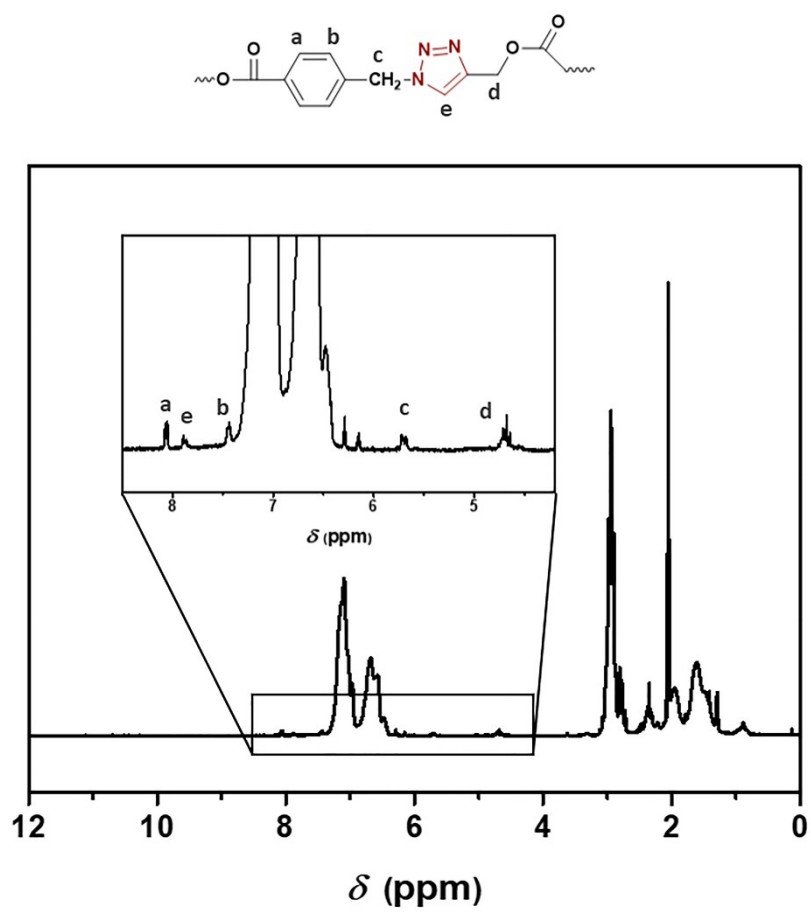


Figure S2 ¹H-NMR spectrum (acetone-*d*₆) of PS-*b*-PVDF-*b*-PS synthesized using azide terminated PVDF

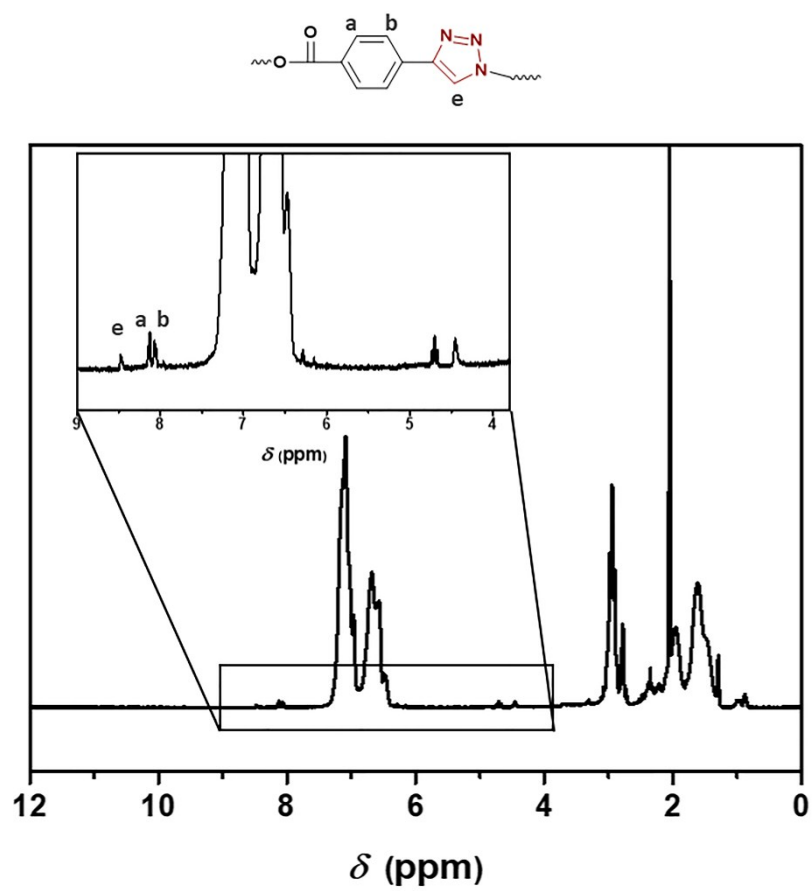


Figure S3 ^1H -NMR spectrum (acetone- d_6) of PS-*b*-PVDF-*b*-PS synthesized using alkyne terminated PVDF

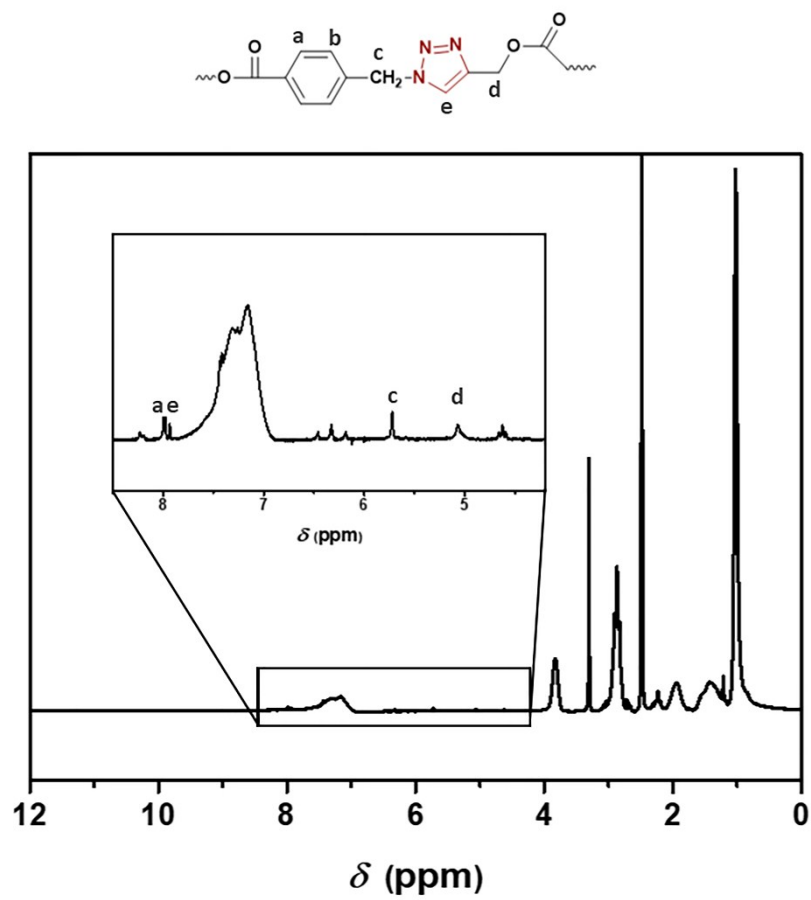


Figure S4 ^1H -NMR spectrum ($\text{DMSO-}d_6$) of PNIPAAm-*b*-PVDF-*b*-PNIPAAm synthesized using azide terminated PVDF

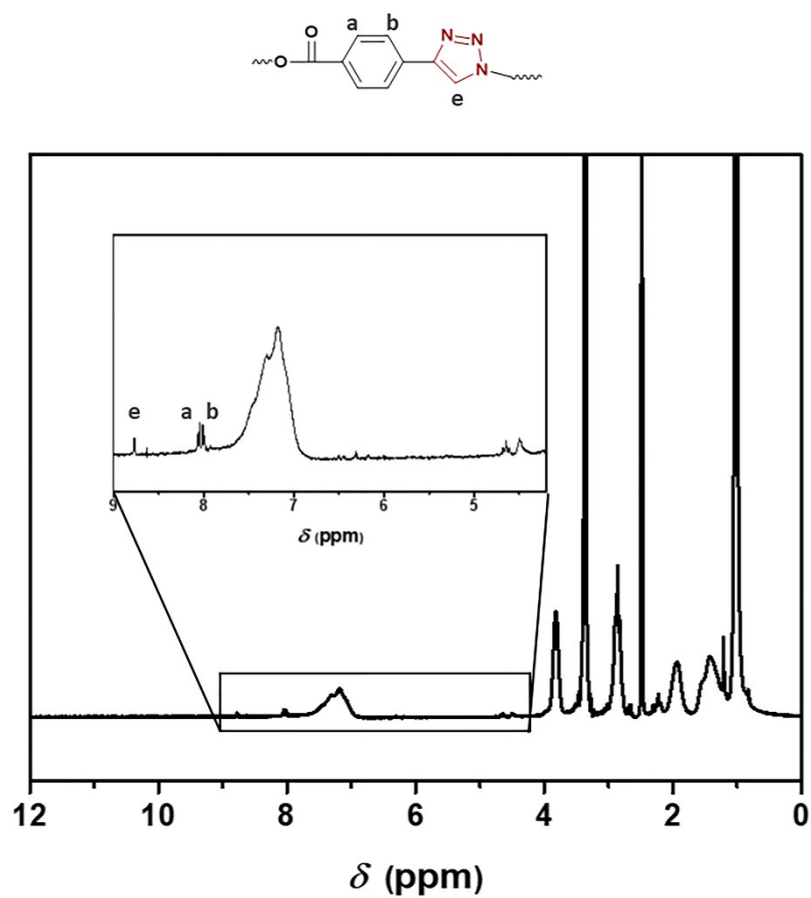


Figure S5 $^1\text{H-NMR}$ spectrum (DMSO- d_6) of PNIPAAm-*b*-PVDF-*b*-PNIPAAm synthesized using alkyne terminated PVDF

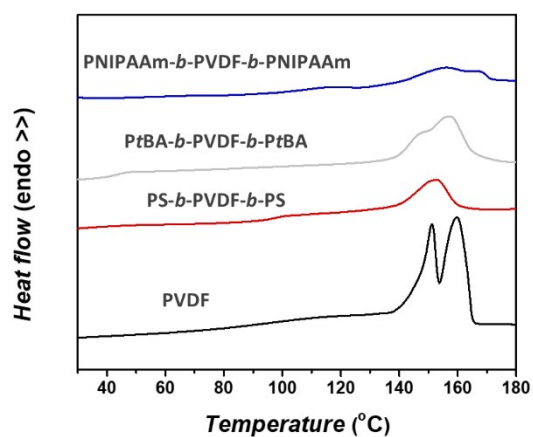


Figure S6 DSC melting curves of PVDF and block copolymers obtained during heating with $10\text{ }^{\circ}\text{C min}^{-1}$

- 1 J. T. Lai, D. Filla and R. Shea, *Macromolecules*, 2002, **35**, 6754–6756.
- 2 R. Ranjan and W. J. Brittain, *Macromol. Rapid Commun.*, 2007, **28**, 2084–2089.
- 3 M. Borsboom, W. Bras, I. Cerjak, D. Detollenaere, D. Glastra van Loon, P. Goedtkindt, M. Konijnenburg, P. Lassing, Y. K. Levine, B. Munneke, M. Oversluizen, R. van Tol and E. Vlieg, *J. Synchrotron Radiat.*, 1998, **5**, 518–520.
- 4 W. Bras, I. P. Dolbnya, D. Detollenaere, R. van Tol, M. Malfois, G. N. Greaves, A. J. Ryan and E. Heeley, *J. Appl. Crystallogr.*, 2003, **36**, 791–794.