Supporting information

Thiourea dioxide as a green and affordable reducing agent for the ARGET ATRP of acrylates, methacrylates, styrene, acrylonitrile and vinyl chloride

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Experimental section

Materials

Alumina (basic, Fisher Scientific), 2-aminoethyl methacrylate hydrochloride (AMA, 95%, Polysciences), copper(II) bromide (CuBr₂, +99% extra pure, anhydrous; Acros), ethyl α-bromoisobutyrate (EBiB 98%, Sigma-aldrich), ethyl α-bromophenylacetate (EBPA, 97% Sigma-Aldrich), bromoform (CHBr₃, +99%; Acros), formamidinesulfonic acid (TDO, 98%, Aldrich), isopropanol (Fisher Scientific), methyl 2-bromopropionate (MBP 98%, Sigma-Aldrich), tris(2-aminoethyl)amine (TREN 96%, Acros), 2-Bromopropionitrile (BPN, Sigma-Aldrich, 97%), and methanol (chemically pure, José Manuel dos Santos, Lda) were used as received.

2,2′-Azobis(2-methylpropionitrile) (AIBN) (98%, Fluka) was purified by recrystallization from methanol before use.

Deionized purified water (Milli-Q®, Millipore, resistivity >18 MΩ.cm) was obtained by reverse osmosis.

Ethanol (EtOH, 96%, José Manuel dos Santos, Lda) and dimethylsulfoxide (DMSO, analytical grade, Fisher Scientific) were dried over calcium hydride, distilled under reduced pressure and stored over molecular sieves.

2-Hydroxyethyl 2-bromoisobutyrate (HEBiB) was synthesized according to procedures described in the literature¹ and distilled under reduced pressure before use.

2-Hydroxyethyl acrylate (HEA) (96%, Sigma-Aldrich) was purified by first dissolving the monomer in water (25% by volume). The solution was extracted with hexane to remove the diacrylates. The aqueous solution was salted (250 g/L NaCl) and the monomer was then separated from the aqueous phase by ether extraction (4 times). Hydroquinone (200 ppm) was used as a radical inhibitor. The organic solvent was removed under reduced pressure. The purified monomer was kept refrigerated and it was passed through a sand/alumina column, in order to remove the radical inhibitor, immediately prior to use.

2-(dimethylamino)ethyl methacrylate (DMAEMA, 98%, Aldrich), methyl acrylate (MA, 99%, Aldrich), methyl methacrylate (MMA, 99%, Aldrich), n-butyl acrylate (n-BA, 100%, Aldrich), poly(ethylene glycol) methyl ether acrylate) (OEOA₄₈₀, Mn = 480;
99% Aldrich), styrene (Sty, 100%, Aldrich) and acrylonitrile (AN, 95% BDH Laboratory Reagents) were passed over a sand/alumina column before use to remove the radical inhibitor.

Tris[2-(dimethylamino)ethyl]amine (Me₆TREN)² and tris(pyridin-2-ylmethyl)amine (TPMA)³ were synthesized as reported in the literature.

VC (99.9%) was kindly supplied by CIRES Lda, Portugal and used as received.

**Techniques**

The $dn/dc$ values of pure polymers were determined using a Rudolph J357 automatic refractometer. Briefly, seven solutions with different concentrations (10, 8, 5, 3, 1, 0.5 and 0 mg.mL⁻¹) were prepared from a 10 mg.mL⁻¹ stock solution of pure polymer in the solvent. The RI of each solution was measured at the desired temperature and the results were plotted versus the concentration. The $dn/dc$ was given by the slope of the curve. $dn/dc_{PDMAEMA} = 0.088$ mL.g⁻¹ in DMF (with 0.03% LiBr) at 60 °C ($R^2 = 0.9926$); $dn/dc_{PMMA} = 0.0676$ mL.g⁻¹ in DMF (with 0.03% LiBr) at 60 °C ($R^2 = 0.9950$); $dn/dc_{PBA} = 0.0671$ mL.g⁻¹, in THF at 30 °C, ($R^2 = 0.9919$); $dn/dc_{POEOA} = 0.0634$ mL.g⁻¹, in THF at 30 °C, ($R^2 = 0.9932$).

The molecular weight parameters of PMA, PVC, PS, PMA-b-PS, PMA-b-PVC-b-PMA, PMA-b-PBA and PBA were determined by high-performance size exclusion chromatography HPSEC; Viscotek (Viscotek TDOAmax) with a differential viscometer (DV), right-angle laser-light scattering (RALLS, Viscotek), low-angle laser-light scattering (LALLS, Viscotek) and RI detectors. The column set consisted of a PL 10 mm guard column (50 x 7.5 mm²) followed by one Viscotek T200 column (6 µm), one Viscotek T3000 column (6 µm) and one Viscotek LT4000L column (7 µm). HPLC dual piston pump was set with a flow rate of 1 mL.min⁻¹. The eluent (THF) was previously filtered through a 0.2 µm filter. The system was also equipped with an on-line degasser. The tests were done at 30 °C using an Elder CH-150 heater. Before the injection (100 µL), the samples were filtered through a nylon membrane with 0.2 µm pore. The system was calibrated with narrow polystyrene standards. Molecular weight ($M_n^{SEC}$) and $D$ ($M_w/M_n$) of the synthesized polymers were determined by Multidetectors calibration.
(dn/dc \text{ PVC} = 0.105 \text{ mL.g}^{-1}; \ dn/dc \text{ PS} = 0.185 \text{ mL.g}^{-1}; \ dn/dc \text{ PMA} = 0.063 \text{ mL.g}^{-1})^4 \text{ using the OmniSEC software version: 4.6.1.354.}

The chromatographic parameters of PHEA, PMMA, PDMAEMA were determined using a size exclusion chromatography (SEC) set-up from Viscotek (Viscotek TDOAmax) equipped with a differential viscometer (DV) and right-angle laser-light scattering (RALLS, Viscotek) and refractive index (RI) detectors. The column set consisted of a PLgel 5 µm guard column followed by one Viscotek T5000 column, one Viscotek T4000 column. A dual piston pump was set with a flow rate of 1 mL/min. The eluent (DMF with 0.03% LiBr) was previously filtered through a 0.2 µm filter. The system was also equipped with an on-line degasser. The tests were done at 60 °C using an Elder CH-150 heater. Before the injection (100 µL), the samples were filtered through a PTFE membrane with 0.2 µm pore. The system was calibrated with narrow poly(methyl methacrylate) standards. Molecular weight ($M_n^{\text{SEC}}$) and dispersity ($D = M_w/M_n$) of the synthesized polymers were determined by multidetectors calibration using the OmniSEC software version: 4.6.1.354 ($dn/dc \text{ PHEA} = 0.0778 \text{ mL.g}^{-1}$)$^5$

The molecular weight of PAMA was determined by aqueous SEC system equipped with an online degassser, a RI detector and a set of columns: Shodex OHpak SB-G guard column, OHpak SB-804HQ and OHpak SB-802.5HQ columns. The polymers were eluted at a flow rate of 0.5 mL/min with 0.1 M Na$_2$SO$_4$ (aq)/1 wt% acetic acid/0.02% NaN$_3$ at 40 °C. Before the injection, the samples were filtered through a PTFE membrane with 0.2 µm pore. The system was calibrated with five narrow poly(ethylene glycol) standards and the polymers molecular weights ($M_n^{\text{SEC}}$) and $D (M_w/M_n)$ were determined by conventional calibration using the Clarity software version 2.8.2.648.

400 MHz $^1$H nuclear magnetic resonance (NMR) spectra of reaction mixture samples were recorded on a Bruker Avance III 400 MHz spectrometer, with a 5-mm TIX triple resonance detection probe, in D$_2$O. Conversions of the monomer were determined by integration of monomer and polymer peaks using MestReNova software version: 6.0.2-5475.

The PMA-Br sample was dissolved in THF at a concentration of 10 mg/mL for the MALDI-TOF-MS analysis. HABA (0.08M in THF) was used as matrix. The dried-droplet sample preparation technique was used to obtain a 1:1 ratio (sample/matrix); an aliquot of 1 µL of each sample was directly spotted on the MTP AnchorChip TM
600/384 TF MALDI target, BrukerDaltonik (Bremen Germany) and, before the sample dried, 70 1 μL of matrix solution in THF was added and the mixture allowed to dry at room temperature, to allow matrix crystallization. External mass calibration was performed with a peptide calibration standard (PSCII) for the range 500-9000 (9 mass calibration points), 0.5 μL of the calibration solution and 75 matrix previously mixed in Eppendorf tube (1:2, v/v) were applied directly on the target and allowed to dry at room temperature. Mass spectra were recorded using an Autoflex III smartbeam MALDI-TOF-MS mass spectrometer BrukerDaltonik (Bremen, Germany) operating in the linear and reflectron positive 80 ion mode. Ions were formed upon irradiation by a smartbeam laser using a frequency of 200 Hz. Each mass spectrum was produced by averaging 2500 laser shots collected across the whole sample spot surface by screening in the range m/z 500–9500. The laser irradiance was set to 35–40 % (relative scale 0- 85 100) arbitrary units according to the corresponding threshold required for the applied matrix systems.

The UV/Vis studies were performed with a Jasco V-530 spectrophotometer. The measurements were carried out in the 200–1100 nm range at room temperature (rt).

The concentration of copper in a PMA-Br macroinitiator was determined by atomic absorption (lower detection limit of 0.002 ppm).

**Procedures**

**Typical synthesis of PMA-Br by TDO-mediated ARGET ATRP**

Different kinetic studies were conducted using MA as the model monomer, in which the ratio of catalyst and solvent was changed. Briefly, MA (6.6 g, 76.47 mmol), CuBr₂ (7.7 mg, 34 μmol), Me₆TREN (19.8 mg, 86 μmol), EBiB (68.6 mg, 334 μmol) and EtOH/H₂O = 90/10 (v/v) (3.5 mL) were added to a 25 mL Schlenk flask equipped with a rare-earth magnetic stirrer bar. Next, TDO (38.0 mg, 334 μmol) was added to the Schlenk flask, which was sealed with a glass stopper, deoxygenated with four freeze-vacuum-thaw cycles and purged with nitrogen. The flask was placed in a water bath at 30 °C and the reaction was allowed to proceed. Different reaction mixture samples were collected during the polymerization. The samples were analyzed by ¹H NMR spectroscopy, to determine the monomer conversion and by SEC, to determine the molecular weight and dispersity of the polymers. The final reaction mixture was diluted
with THF and passed through an alumina column to remove copper. The pure PMA-Br was recovered after precipitation in cold methanol, followed by drying under reduced pressure.

**Typical synthesis of PBA-Br by TDO-mediated ARGET ATRP**

$n$-BA (2.7 g, 20.9 mmol), CuBr$_2$ (2.1 mg, 9 μmol), Me$_6$TREN (5.4 mg, 24 μmol), EBiB (18.8 mg, 94 μmol) and EtOH/H$_2$O = 90/10 (v/v) (1.5 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stirrer bar. Next, TDO (10.4 mg, 94 μmol) was added to the Schlenk flask, which was sealed with a glass stopper, deoxygenated with four freeze-vacuum-thaw cycles and purged with nitrogen. The flask was placed in a water bath at 30 °C and the reaction was allowed to proceed. Different reaction mixture samples were collected during the polymerization. The samples were analyzed by $^1$H NMR spectroscopy, to determine the monomer conversion and by SEC, to determine the molecular weight and dispersity of the polymers. The final reaction mixture was diluted with THF and passed through an alumina column to remove copper. The pure PBA-Br was recovered after precipitation in cold methanol, followed by drying under reduced pressure.

**Typical synthesis of PS-Br by TDO-mediated ARGET ATRP**

Sty (2.7 g, 26.0 mmol), CuBr$_2$ (2.6 mg, 12 μmol), Me$_6$TREN (6.8 mg, 29 μmol), EBiB (23.4 mg, 118 μmol) and DMF (1.5 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stirrer bar. Next, TDO (13.0 mg, 118 μmol) was added to the Schlenk flask, which was sealed with a glass stopper, deoxygenated with four freeze-vacuum-thaw cycles and purged with nitrogen. The flask was placed in a water bath at 30 °C and the reaction was allowed to proceed. Different reaction mixture samples were collected during the polymerization. The samples were analyzed by $^1$H NMR spectroscopy, to determine the monomer conversion and by SEC, to determine the molecular weight and dispersity of the polymers. The final reaction mixture was diluted with THF and passed through an alumina column to remove copper. The pure PS-Br was recovered after precipitation in cold methanol, followed by drying under reduced pressure.
Typical synthesis of PHEA-Br by TDO-mediated ARGET ATRP

HEA (2.7 g, 23.0 mmol), CuBr$_2$ (2.3 mg, 10 μmol), Me$_6$TREN (6.0 mg, 26 μmol), EBiB (20.7 mg, 104 μmol) and EtOH/H$_2$O = 90/10 (v/v) (1.5 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stirrer bar. Next, TDO (11.5 mg, 104 μmol) was added to the Schlenk flask, which was sealed with a glass stopper, deoxygenated with four freeze-vacuum-thaw cycles and purged with nitrogen. The flask was placed in a water bath at 30 °C and the reaction was allowed to proceed. Different reaction mixture samples were collected during the polymerization. The samples were analyzed by $^1$H NMR spectroscopy, to determine the monomer conversion and by SEC, to determine the molecular weight and dispersity of the polymers. The pure PHEA-Br was recovered after dialysis against water (c.o. = 3500), followed by freeze-drying.

Typical synthesis of PMMA-Br by TDO-mediated ARGET ATRP

MMA (2.8 g, 27.8 mmol), CuBr$_2$ (2.8 mg, 13 μmol), Me$_6$TREN (7.2 mg, 31 μmol), EBiB (25.0 mg, 126 μmol) and EtOH/H$_2$O = 90/10 (v/v) (1.5 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stirrer bar. Next, TDO (13.9 mg, 126 μmol) was added to the Schlenk flask, which was sealed with a glass stopper, deoxygenated with four freeze-vacuum-thaw cycles and purged with nitrogen. The flask was placed in a water bath at 30 °C and the reaction was allowed to proceed. Different reaction mixture samples were collected during the polymerization. The samples were analyzed by $^1$H NMR spectroscopy, to determine the monomer conversion and by SEC, to determine the molecular weight and dispersity of the polymers. The final reaction mixture was diluted with THF and passed through an alumina column to remove copper. The pure PMMA-Br was recovered after precipitation in cold methanol, followed by drying under reduced pressure.

Typical synthesis of PDMAEMA-Br by TDO-mediated ARGET ATRP

DMAEMA (2.8 g, 17.3 mmol), CuBr$_2$ (1.7 mg, 8 μmol), Me$_6$TREN (4.5 mg, 20 μmol), EBiB (15.6 mg, 78 μmol) and EtOH/H$_2$O = 90/10 (v/v) (1.5 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stirrer bar. Next, TDO (8.6 mg, 78 μmol) was added to the Schlenk flask, which was sealed with a glass stopper, deoxygenated with four freeze-vacuum-thaw cycles and purged with nitrogen. The flask was placed in a
water bath at 30 °C and the reaction was allowed to proceed. Different reaction mixture samples were collected during the polymerization. The samples were analyzed by $^1$H NMR spectroscopy, to determine the monomer conversion and by SEC, to determine the molecular weight and dispersity of the polymers. The pure PDMAEMA-Br was recovered after dialysis against water (c.o. = 3500), followed by freeze-drying.

**Typical synthesis of PAMA-Br by TDO-mediated ARGET ATRP**

AMA (0.5 g, 2.9 mmol), CuBr$_2$ (3.2 mg, 14.3 μmol), TPMA (16.7 mg, 57.4 μmol), EBPA (7.2 mg, 28.7 μmol) and IPA/H$_2$O = 90/10 (v/v) (1.43 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stirrer bar. Next, TDO (3.2 mg, 28.7 μmol) was added to the Schlenk flask, which was sealed with a glass stopper, deoxygenated with four freeze-vacuum-thaw cycles and purged with nitrogen. The flask was placed in a water bath at 30 °C and the reaction was allowed to proceed. Different reaction mixture samples were collected during the polymerization. The samples were analyzed by $^1$H NMR spectroscopy, to determine the monomer conversion and by SEC, to determine the molecular weight and dispersity of the polymers. The pure PAMA-Br was recovered after dialysis against water (c.o. = 3500), followed by freeze-drying.

**Typical synthesis of PAN-Br by TDO-mediated ARGET ATRP**

AN (2.0 g, 38.2 mmol), CuBr$_2$ (3.8 mg, 17.2 μmol), TPMA (12.5 mg, 43.0 μmol), BPN (23.7 mg, 172 μmol), DMF for NMR internal standard (0.19 ml) and DMSO (3.75 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stirrer bar. Next, TDO (19.0 mg, 172 μmol) was added to the Schlenk flask, which was sealed with a glass stopper, deoxygenated with four freeze-vacuum-thaw cycles and purged with nitrogen. The flask was placed in a water bath at 30 °C and the reaction was allowed to proceed. Different reaction mixture samples were collected during the polymerization. The samples were analyzed by $^1$H NMR spectroscopy, to determine the monomer conversion and by SEC, to determine the molecular weight and dispersity of the polymer. The pure PAN-Br was recovered after precipitation in a cold mixture of MeOH/H$_2$O = 50/50 (v/v), followed by drying under reduced pressure.
Typical synthesis of Br-PVC-Br by TDO-mediated ARGET ATRP

A 50 mL Ace glass 8645#15 pressure tube, equipped with bushing and plunger valve, was charged with a mixture of CHBr₃ (83.8 mg, 0.33 mmol), CuBr₂ (36.3 mg, 0.16 mmol), TREN (49.5 mg, 0.33 mmol), and DMSO/H₂O = 95/5 (v/v) (5 mL) (previously bubbled with nitrogen for about 15 min). TDO (35.8 mg, 0.33 mmol) and the precondensed VC (5 mL, 72.1 mmol) were added to the tube. The exact amount of VC was determined gravimetrically. The tube was closed, submerged in liquid nitrogen and degassed through the plunger valve by applying reduced pressure and filling the tube with N₂ about 20 times. The valve was closed, and the tube reactor was placed in a water bath at 42 °C with stirring (700 rpm). After 48 h, the reaction was stopped by plunging the tube into ice water. The tube was slowly opened, the excess VC was evaporated inside a fume hood, and the mixture was precipitated into methanol. The polymer was separated by filtration and dried in a vacuum oven until constant weight to produce. The polymer was separated by filtration and dried in a vacuum oven until constant weight, yielding 0.50 g (11.0 %) of PVC ($M_n^{SEC} = 3.1 \times 10^3$, $D = 1.60$).

Synthesis of PMA-b-PS-Br block copolymer by TDO-mediated ARGET ATRP

Sty (1 mL, 8.7 mmol), CuBr₂ (0.6 mg, 2 μmol), Me₆TREN (1.4 mg, 6 μmol), and PMA-Br (119.3 mg, 25 μmol) were dissolved in HPLC DMF (1.00 mL), in a 10 mL Schlenk flask, equipped with a rare-earth magnetic stirrer bar. Next, TDO (2.7 mg, 25 μmol) was added to the Schlenk flask, which was sealed with a glass stopper, deoxygenated with four freeze-vacuum-thaw cycles and purged with nitrogen. The flask was placed in an oil bath at 70 °C and the reaction was allowed to proceed. The reaction was stopped after 22.5 h (conv.Sty = 50%). The final reaction mixture was diluted with THF and passed through an alumina column to remove copper. The pure PMA-b-PS-Br was recovered after precipitation in cold methanol, followed by drying under reduced pressure. The chemical structure of the copolymer was confirmed by ¹H NMR spectroscopy and the molecular weight and dispersity were determined by SEC.
Synthesis of PMA-b-PVC-b-PMA block copolymer by TDO-mediated ARGET ATRP

The Br-PVC-Br macrominitiator conversion ($M_n^{th} = 1790$, $M_n^{SEC} = 3.1 \times 10^3$, $D = 1.60$) obtained at 11.0% monomer was obtained following the previously described procedure. After precipitation in methanol, the polymer was dissolved in THF and reprecipitated in methanol. The polymer was dried under vacuum until constant weight. A mixture of MA (3.0 mL, 32.8 mmol), CuBr$_2$ (1.0 mg, 5 μmol), Me$_6$TREN (2.8 mg, 12 μmol), Br-PVC-Br macrominiator ($M_n^{SEC} = 3.1 \times 10^3$, $D = 1.60$, 147 mg, 0.047 mmol), previously dissolved in DMSO/H$_2$O = 95/5 (v/v) (3.0 mL), was added to a 10 mL Schlenk flask equipped with a rare-earth magnetic stirrer bar. Next, TDO (5.2 mg, 0.047 mmol) was added to the Schlenk flask, which was sealed with a glass stopper, deoxygenated with four freeze-vacuum-thaw cycles and purged with nitrogen. The flask was placed in a water bath at 30 °C and the reaction was allowed to proceed. The reaction was stopped after 7 h and the mixture was analyzed by $^1$H NMR spectroscopy to determine the MA conversion (59.8%) and by SEC to determine the molecular weight of the resulting PMA-b-PVC-b-PMA block copolymer ($M_n^{SEC} = 39.7 \times 10^3$ and $D = 1.30$).

Synthesis of PMA-b-PBA-Br by “one-pot” chain extension by TDO-mediated ARGET ATRP

MA (2.1 g, 21.8 mmol), CuBr$_2$ (8.1 mg, 36.4 μmol), Me$_6$TREN (21.0 mg, 91.0 μmol), EBiB (72.5 mg, 36.4 μmol) and EtOH/H$_2$O = 90/10 (v/v) (1 mL) were added to a 10 mL Schlenk flask equipped with a rare-earth magnetic stirrer bar. Next, TDO (40.2 mg, 36.4 μmol) was added to the Schlenk flask, which was sealed with a glass stopper, deoxygenated with four freeze-vacuum-thaw cycles and purged with nitrogen. The flask was placed in a water bath at 30 °C. After 4h, the (conv.$_{MA} = 81\%$), degassed n-BA (5.8 g, 36.4 mmol) was injected in the reaction mixture, under nitrogen flow, and the polymerization was allowed to proceed for further 18.4h (conv.$_{n-BA} = 97\%$). The final reaction mixture was diluted with THF and passed through an alumina column to remove copper. The pure PMA-b-PBA-Br was recovered after precipitation in cold methanol, followed by drying under reduced pressure. The chemical structure of the
copolymer was confirmed by $^1$H NMR spectroscopy and the molecular weight and dispersity were determined by SEC.

**UV-Vis spectra**

![Figure S1](image.png)

**Figure S1.** UV-Vis spectra showing the reduction of CuBr$_2$ by TDO in different solvent mixtures mimicking polymerization conditions. Conditions: [TDO]$_0$/[CuBr$_2$]$_0$/[Me$_6$TREN]$_0 = 1/0.1/0.25$ (molar); [CuBr$_2$]$_0 = 0.01$ mmol/mL; T = 30 °C.

**Polymerization details**

**Table S1.** Polymerization of MA by TDO/CuBr$_2$/Me$_6$TREN-catalyzed ATRP using different [TDO]$_0$. Conditions: [MA]$_0$/[EBiB]$_0$/[TDO]$_0$/[CuBr$_2$]$_0$/[Me$_6$TREN]$_0 = 222/1/[TDO]_0/0.1/0.25$, EtOH/H$_2$O $= 90/10$ (v/v); [MA]$_0$/[solvent]$_0 = 2/1$ (v/v); T = 30 °C

| Entry | [TDO]$_0$ | $k_p$ (h$^{-1}$) | Induction time (h) | Conv. (%) | $M_n$ (g/mol) | $M_n^{SEC}$ (g/mol) | $D$ |
|-------|-----------|-----------------|-------------------|-----------|---------------|-------------------|------|
| 1     | 2         | 1.01            | 0.8               | 88        | 17.0          | 17.4              | 1.12 |
| 2     | 1         | 0.56            | 0.4               | 76        | 14.8          | 14.6              | 1.04 |
| 3     | 0.2       | 0.49            | 0.2               | 72        | 14.1          | 15.5              | 1.02 |

*a* In comparison to the number of moles of EBiB; *b* Reaction time = 3 h
Table S2. Monomer conversion and molecular weight parameters of PMA obtained by free radical polymerization at 70 °C, in the absence and presence of TDO. Conditions: solvent – EtOH/H₂O = 90/10 (v/v); [M]/[solvent] = 2/1 (v/v).

| Entry | Conditions | Time (h) | Conv. (%) | $M_n$ SEC x $10^{-3}$ | $D$ |
|-------|-------------|----------|------------|-------------------------|-----|
| 1     | [MA]₀/[AIBN]₀/[TDO]₀ = 222/0.2/2 | 0.33     | 11         | 82.4                    | 3.37|
| 2     | [MA]₀/[AIBN]₀/[TDO]₀ = 222/0.2/0 | 0.25     | 69         | 171.5                   | 1.85|

Table S3. Experimental conditions and molecular weight results for the model experiments to investigate the mechanism of the MA polymerization. Conditions: solvent – EtOH/H₂O = 90/10 (v/v); T = 30 °C.

| Molar | Entry | MA | EBiB | PMA-Br | CuBr₂ | TDO | Me₆TREN | t (h) | Conv. (%) | $M_n$ SEC x $10^{-3}$ | $D$ |
|-------|-------|----|------|--------|-------|-----|---------|-------|-----------|-----------------------|-----|
|        | 1     | 222  | 0    | 0      | 1     | 0   | 16.3    | 0     | 0         | *a*                   | *a* |
|        | 2     | 222  | 1    | 0      | 0.1   | 0   | 0.25    | 25    | 0         | *a*                   | *a* |
|        | 3     | 222  | 1    | 0      | 0     | 1   | 5.2     | 0     | *a*       | *a*                   | *a* |
|        | 4     | 222  | 1    | 0      | 0     | 1   | 0       | 22    | 96        | 418                   | 1.54|
|        | 5     | 222  | 0    | 1      | 0     | 1   | 0       | 21.0  | 0         | *b*                   | *b* |
|        | 6     | 222  | 1c   | 0      | 0     | 1   | 5       | 0     | *a*       | *a*                   | *a* |
|        | 7     | 222  | 1c   | 0      | 0     | 1   | 22      | 93    | 425       | 1.78                  |     |
|        | 8d    | 222  | 1    | 0      | 0     | 1   | 0       | 17    | 48        | 310                   | 1.93|

*a* No SEC trace detected; *b* Same SEC trace as the one of PMA-Br macroinitiator; *c* MBP was used as the initiator; *d* Experiment conducted in the dark.
Table S4. Experimental conditions and molecular weight results for the model experiments to investigate the mechanism of the VC polymerization. Conditions: solvent – DMSO/H$_2$O = 95/5 (v/v); T = 42 °C.

| Entry | VC | CHBr$_3$ | Br-PVC-Br | TDO | CuBr$_2$ | TREN | t (h) | Conv. (%) | $M_n^{SEC}$ x 10$^{-3}$ | $D$ |
|-------|----|----------|------------|-----|---------|------|------|-----------|-----------------|------|
| 1     | 222| 1        | 0          | 0   | 0.5     | 1    | 48   | 0         | .a              | .a   |
| 2     | 222| 0        | 0          | 1   | 0       | 0    | 48   | 0         | .a              | .a   |
| 3     | 700| 0        | 1          | 1   | 0       | 1    | 48   | 0         | .**             | .**  |
| 4     | 222| 1        | 0          | 0   | 0       | 0    | 6    | 0         | .a              | .a   |
| 5     | 222| 1        | 0          | 1   | 0       | 0    | 48   | 10        | 19.8            | 2.28 |

*a No SEC trace detected; b Same SEC trace as the one of Br-PVC-Br macroinitiator.

Table S5. Results for the polymerization of MA at 30 °C by ARGET ATRP using different reducing agents. Conditions: [MA]$_0$/[EBiB]$_0$/[reducing agent]$_0$/[CuBr$_2$]$_0$/[Me$_6$TREN]$_0$ = 222/1/1/0.1/0.25 in EtOH/H$_2$O = 90/10 (v/v).

| Entry | Reducing agent | $k_p^{app}$ (h$^{-1}$) | Time (h) | Conv. (%) | $M_n^{th}$ x 10$^{-3}$ | $M_n^{SEC}$ x 10$^{-3}$ | $D$ |
|-------|----------------|------------------------|----------|-----------|------------------------|--------------------------|------|
| 1     | TDO            | 0.56                   | 3        | 76        | 14.8                   | 14.6                     | 1.04 |
| 2     | Ascorbic acid  | 0.61                   | 3        | 77        | 14.9                   | 17.1                     | 1.13 |
| 3     | Glucose        | -                      | 47       | 10        | 2.0                    | 1.90                     | 1.09 |
Figure S2. Kinetic plots of (a) monomer conversion and $\ln[M_0]/[M]$ vs. time and (b) $M_n^{SEC}$ and $M_w/M_n$ vs. $M_n^{th}$ conversion and (c) chromatograms in THF for the TDO/CuBr$_2$/TREN-catalyzed ARGET ATRP of VC in DMSO/H$_2$O = 95/5 (v/v). Conditions: $[VC]_0/[CHBr_3]_0/[TDO]_0/[CuBr_2]_0/[TREN]_0 = 222/1/1/0.5/1$, $[VC]_0/[solvent]_0 = 1/1$ (v/v); $T = 42 \, ^\circ\text{C}$.

Figure S3. Kinetic plots of (a) $\ln[M_0]/[M]$ vs. time and (b) $M_n^{SEC}$ and $M_w/M_n$ vs. monomer conversion for the TDO/CuBr$_2$/Me$_6$TREN-catalyzed ARGET ATRP of Sty in DMF at 70 °C. Conditions: $[Sty]_0/[EBiB]_0/[TDO]_0/[CuBr_2]_0/[Me_6TREN]_0 = 220/1/1/0.1/0.25$, $[Sty]_0/[solvent]_0 = 2/1$ (v/v); $T = 70 \, ^\circ\text{C}$.
Figure S4. Kinetic plots of (a) $\ln[M]_0/[M]$ vs. time and (b) $M_n^{\text{SEC}}$ and $M_w/M_n$ vs. monomer conversion for the TDO/CuBr$_2$/TPMA-catalyzed ARGET ATRP of AN in DMSO at 30 °C. Conditions: $[\text{AN}]_0/[\text{BPN}]_0/[\text{TDO}]_0/[\text{CuBr}_2]_0/[\text{TPMA}]_0 = 195/1/1/0.1/0.25$, $[\text{AN}]_0/[\text{solvent}]_0 = 1/1.5$ (v/v); $T = 30^\circ$C.

Chromatograms

Figure S5. SEC traces of Br-PVC-Br macroinitiator (red line) and PMA-$b$-PVC-$b$-PMA block copolymer (black line) obtained after chain extension by TDO-mediated ATRP at 30 °C.
\(^1\)H NMR spectra

**Figure S6.** \(^1\)H NMR spectrum, in CDCl\(_3\), of a PMA-Br with 98\% chain-end functionality obtained at 98\% conversion \((M_n^{\text{NMR}} = 4.8 \times 10^3; M_n^{\text{th}} = 4.9 \times 10^3; M_n^{\text{SEC}} = 4.8 \times 10^3; D = 1.06)\).

**Figure S7.** \(^1\)H NMR spectrum, in D\(_2\)O, of PAMA-Br \((M_n^{\text{th}} = 14.4 \times 10^3; M_n^{\text{SEC}} = 18.0 \times 10^3; D = 1.14)\).
Figure S8. \(^1\)H NMR spectrum, in D\(_2\)O, of PHEA-Br (\(M_n^{th} = 25.3 \times 10^3\); \(M_n^{SEC} = 26.4 \times 10^3\); \(D = 1.13\)).

Figure S9. \(^1\)H NMR spectrum, in CDCl\(_3\), of PMMA-Br (\(M_n^{th} = 17.8 \times 10^3\); \(M_n^{SEC} = 22.0 \times 10^3\); \(D = 1.25\)).
Figure S10. $^1$H NMR spectrum, in CDCl$_3$, of PBA-Br ($M_n^\text{th} = 28.1 \times 10^3$; $M_n^\text{SEC} = 19.8 \times 10^3$; $D = 1.08$).

Figure S11. $^1$H NMR spectrum, in CDCl$_3$, of PDMAEMA-Br ($M_n^\text{th} = 32.2 \times 10^3$; $M_n^\text{SEC} = 26.5 \times 10^3$; $D = 1.26$).
Figure S12. $^1$H NMR spectrum, in CDCl$_3$, of PS-Br ($M_n^{th} = 3.1 \times 10^3$; $M_n^{SEC} = 2.4 \times 10^3$; $D = 1.08$).

Figure S13. $^1$H NMR spectrum, in THF-$d_8$, of Br-PVC-Br ($M_n^{th} = 1.8 \times 10^3$; $M_n^{SEC} = 3.1 \times 10^3$; $D = 1.60$).
Figure S14. $^1$H NMR spectrum, in DMSO-$d_6$, of PAN-Br ($M_n^{th} = 3.8 \times 10^3$; $M_n^{SEC} = 6.58 \times 10^3$; $D = 1.22$).

Figure S15. $^1$H NMR spectrum, in CDCl$_3$, of PMA-$b$-PS-Br ($M_n^{th} = 20.4 \times 10^3$; $M_n^{SEC} = 26.1 \times 10^3$; $D = 1.32$).
Figure S16. $^1$H NMR spectrum, in CDCl$_3$, of PMA-$b$-PBA-Br ($M_n^{th} = 17.9 \times 10^3; M_n^{SEC} = 18.1 \times 10^3; D = 1.07$).

Figure S17. $^1$H NMR spectrum, in THF-$d_8$, of Br-PMA-$b$-PVC-$b$-PMA-Br ($M_n^{th} = 39.2 \times 10^3; M_n^{SEC} = 39.7 \times 10^3; D = 1.30$).
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