Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

A New Paradigm in Polymerization Induced Self-Assembly (PISA): Exploitation of "Non-Living" Addition-Fragmentation Chain Transfer (AFCT) Polymerization

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Experimental

Materials

Benzyl methacrylate (BzMA, Sigma-Aldrich), poly(ethylene glycol) methyl ether methacrylate (PEGMA, M_n = 300 g mol^{-1}, Sigma-Aldrich), Methyl 2-(bromomethyl)acrylate (MBMA, Sigma-Aldrich), 4,4'-azobis(4-cyanovaleric acid) (ACVA, ≥99%, Sigma-Aldrich) were used as received. 1,1'-azobis(1-cycohezanenitrile) (ACN, Sigma-Aldrich) was purified by recrystallization from methanol. Toluene (99.5%, Univar), ethanol (100%, Chem-Supply Pty Ltd), Deuterated chloroform ($CDCl_3$, 99.8%, Cambridge Isotope Laboratories) were used as received. All other reagents were used as received unless otherwise specified.

Instrumentation

^{1}H NMR Spectroscopy: All NMR spectra were recorded using a 400 MHz Bruker Avance-400 spectrometer in $CDCl_3$.

Gel Permeation Chromatography (GPC): Molecular weights and molecular weight distributions (MWDs) were determined by GPC employing a Shimadzu modular system with dimethylacetamide containing 0.03%w/v LiBr and 0.05% w/v 2,6-dibutyl-4-methylphenol (BHT) as eluent at 50 ^{o}C at a flow rate of 1.0 mL/min with injection volume of 100 μL. The GPC was equipped with a DGU-12A solvent degasser, a LC-10AT pump, a CTO-10A column oven and an RID-10A refractive index detector, and a Polymer Laboratories 5.0 μm bead-size guard column (50×7.5 mm) followed by four linear Styragel columns. The system was calibrated against poly(methyl methacrylate) standards ranging from 500 to 10^5 g/mol.

Dynamic Light Scattering (DLS): DLS measurements were performed using a Malvern Zetasizer Nano Series running DTS software and using a 4mW He-Ne laser operating at a wavelength of 633nm and an avalanche photodiode (APD) detector. The scattered light was detected at an angle of 173^o at 25 °C. The raw dispersions after polymerization were diluted with ethanol to give 0.5-1 mg/ml dispersions.

Transmission Electron Microscopy (TEM): The size and morphologies of the nanoparticles were observed using a JEOL1400 TEM at an accelerating voltage of 100 kV. One drop of the raw nanoparticle dispersion sample was deposited onto carbon-coated copper grids (ProSciTech). 2% uranyl acetate solution was applied to all samples as negative staining.

Synthesis of PEGMA macroAFCT via AFCT polymerization

In a typical experiment, a vial was charged with PEGMA (9 g, 30 mmol), MBMA (228.1 mg, 1.274 mmol), ACN (62.3 mg, 0.2548 mmol), and 1,3,5-trioxane (189.2 mg, 2.1 mmol) as internal standard for determination of the monomer conversion by ^{1}H NMR in toluene (10 ml). The solution was poured into a septum-sealed round bottomed flask, purged for 30 min with nitrogen in an ice-water bath and heated to 80 ^{o}C in a thermos-stated oil bath under magnetic stirring. The polymerization was quenched after 4.5 h by immersion of the flask in ice/water. The individual monomer conversion was determined by ^{1}H NMR spectroscopy in $CDCl_3$ by the relative integration of the protons of 1,3,5-trioxane and the vinylic protons of monomer (overall conversion = 37%). The number average molecular weight

($M_{n,NMR}$) of the macroAFCT was calculated form the following equation

$$Mn,NMR = [(\frac{\int I^{3.45-3.33\ ppm}}{3})/(\frac{\int I^{2.6-2.4\ ppm}}{2})] \times 300 + Mw_{MBMA} = 20.3 \times 300 + 179.0$$
$$= 6269$$

(Fig. S1). DMAc GPC (vs PMMA calibration standards) yielded M_n = 5,896 mol^{-1} and $Đ$ = 1.31. The macroAFCT was purified by dialysis against methanol for 24 h.

AFCT dispersion polymerization

In a typical AFCT dispersion polymerization, BzMA (100 mg, 0.568 mmol; 20% w/w rel. solvent), 4,4'-azobis (4-cyanopentanoic acid) (ACVA, 0.636 mg, 0.00227 mmol) and macroAFCT agent (66.7 mg, 0.01135 mmol) were dissolved in 500 mg of ethanol. The recipes of all polymerization are displayed in Table S1. The solution was added to a 5 ml round bottomed flask which was sealed with a rubber septum and purged with nitrogen for 30 min. Polymerization was commenced by submerging the round bottomed flask in a preheated oil bath at 80 °C for 10, 30, 45 and 60 min, respectively. The macroAFCT: initiator molar ratio was fixed at 5:1 in all cases. The resulting polymer was isolated by precipitation in ethanol followed by centrifuging, to yield PEGMA-*b*-PBzMA as white powder.

Polymer	Time (h)	Conversion (%)	M_n(NMR) (g mol^{-1})	M_n(GPC) (g mol^{-1})	$Đ$
MacroAFCT	4.5	37	6269	5896	1.31

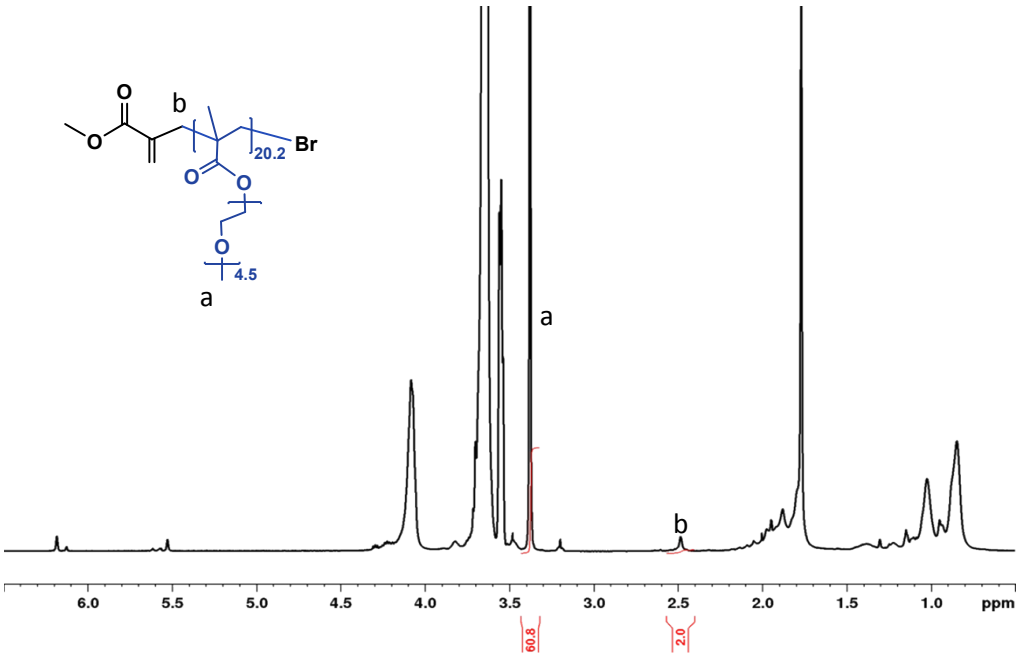

Fig S1. Molecular weight (*M*n), dispersity (*Đ*) values and ^{1}H NMR spectrum of purified PEGMA macroAFCT used in this study.

Table S1. Recipes for addition-fragmentation chain transfer (AFCT) polymerization of benzyl methacrylate in ethanol at 80 °C.

Experiment	Run 1	Run 2	Run 3	Run 4
Initial [BzMA]/[MacroAFCT]	20	50	100	150
BzMA	0.567*(100)#	0.567(100)	0.567(100)	0.567(100)
MacroAFCT	2.83×10^{-2} (167.0)	1.13×10^{-2} (66.7)	5.67×10^{-3} (33.4)	3.78×10^{-3} (22.3)
ACVA	5.66×10^{-3} (1.58)	2.23×10^{-3} (0.63)	1.13×10^{-3} (0.32)	7.56×10^{-4} (0.21)
EtOH	10.85(500)	10.85(500)	10.85(500)	10.85(500)

* Amount (mmol); # Weight (mg)

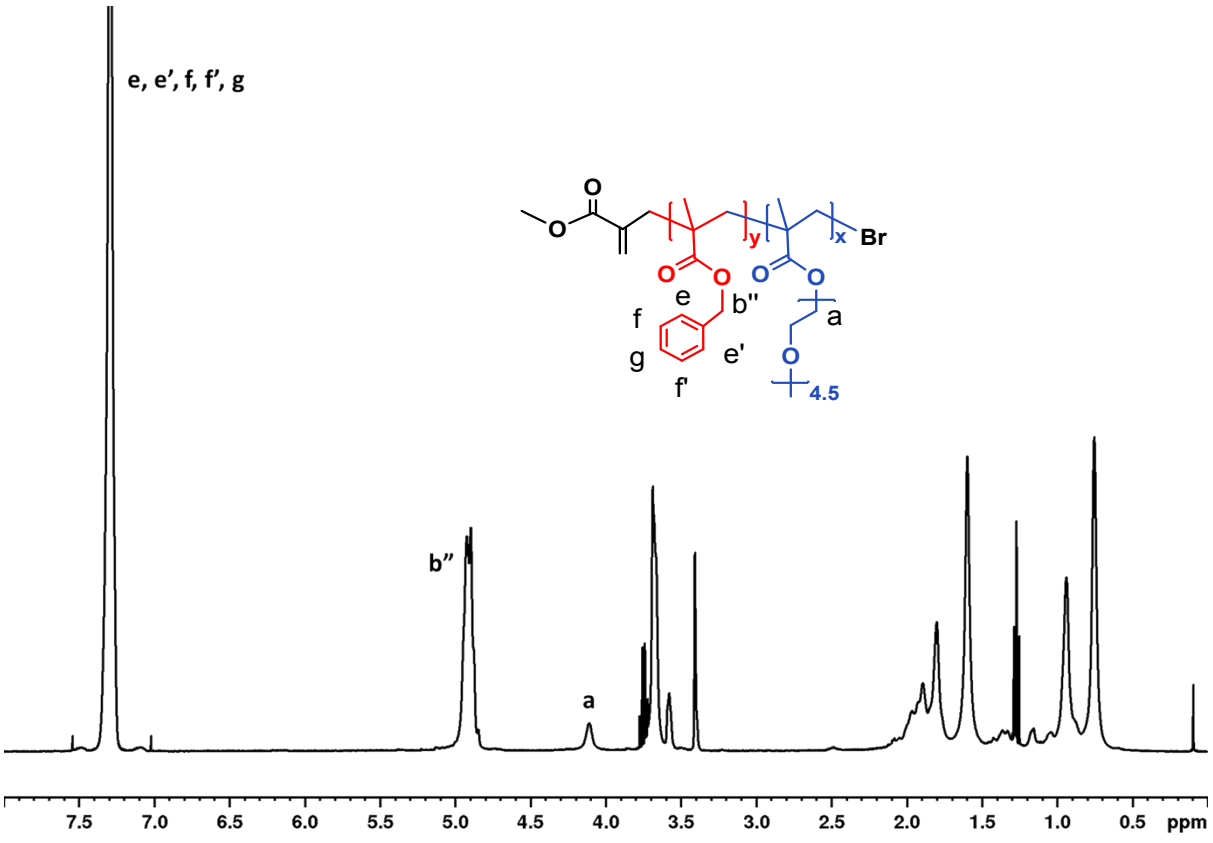

Fig S2. ^{1}H NMR spectrum of purified PEGMA-*b*-PBZMA prepared by AFCT dispersion polymerization of BzMA using PEGMA as macroAFCT ([BzMA]:[MacroAFCT] = 50; 60 min polymerization time). Note that the polymer sample also contains some amount of products from bimolecular termination reactions (*i.e.* polymer not having the ideal structure shown).

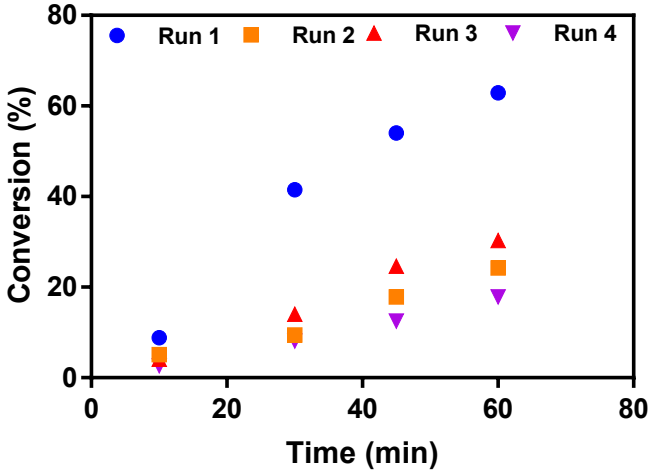

Fig S3. Conversion-time data derived from ^{1}H NMR analyses for AFCT dispersion polymerization of BzMA in ethanol at 80 °C using a PEGMA based macroAFCT agent.

(a)

Experiment	M_n(g/mol)	$Đ$
Run 1	21,300	1.71
Run 2	22,200	1.71
Run 3	26,500	1.73
Run 4	27,300	1.66

(b)

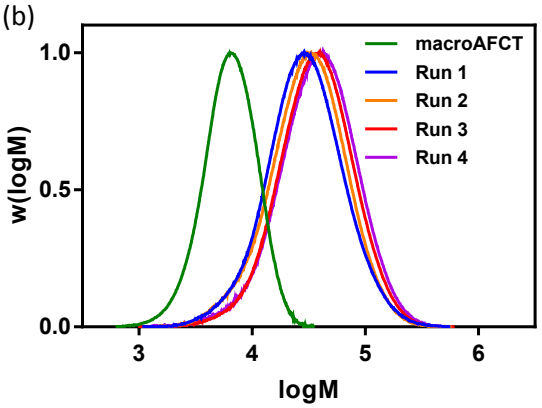

Fig S4. GPC data in the form of (a) M_n and $Đ$ and (b) molecular weight distributions for purified PEGMA-*b*-PBzMA diblock copolymers from AFCT dispersion polymerization of BzMA in ethanol at 80 °C using a PEGMA based macroAFCT agent.