Supporting Information for

Redox-Initiated RAFT Emulsion Polymerization-Induced Self-Assembly of *β*-Ketoester Functional Monomers

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Supporting Figures.

Table S1. Formulation for preparing $PPEGMA_n$-$PAEMA_m$ block copolymer assembiles via redox-initiated RAFT emulsion polymerization.

Monomer Concentration （% w/w）	Target composition	AEMA (g)	Macro-CTA (g)	H_2O (g)	KPS (50 mg/mL in H_2O)	NaAs (50 mg/mL in H_2O)
15	$PPEGMA_{12}$-$PAEMA_{70}$	0.50	0.1988	2.729	60 μL	44 μL
	$PPEGMA_{12}$-$PAEMA_{100}$	1.00	0.2784	5.521	84 μL	62 μL
	$PPEGMA_{12}$-$PAEMA_{125}$	1.50	0.3340	8.326	100 μL	74 μL
	$PPEGMA_{12}$-$PAEMA_{150}$	1.20	0.2227	6.682	68 μL	50 μL
20	$PPEGMA_{12}$-$PAEMA_{70}$	0.60	0.2386	2.276	72 μL	52 μL
	$PPEGMA_{12}$-$PAEMA_{100}$	0.60	0.1670	2.314	50 μL	36 μL
	$PPEGMA_{12}$-$PAEMA_{125}$	1.50	0.3340	5.826	100 μL	74 μL
	$PPEGMA_{12}$-$PAEMA_{150}$	1.00	0.1856	3.902	56 μL	42 μL
25	$PPEGMA_{12}$-$PAEMA_{70}$	1.00	0.3977	2.792	120 μL	88 μL
	$PPEGMA_{12}$-$PAEMA_{100}$	1.20	0.3340	3.426	100 μL	74 μL
	$PPEGMA_{12}$-$PAEMA_{125}$	1.50	0.3340	4.326	100 μL	74 μL
	$PPEGMA_{12}$-$PAEMA_{150}$	1.50	0.2784	4.354	84 μL	62 μL
20	$PPEGMA_{21}$-$PAEMA_{150}$	1.00	0.3186	3.902	56 μL	42 μL
	$PPEGMA_{21}$-$PAEMA_{200}$	1.00	0.2390	3.928	42 μL	30 μL
	$PPEGMA_{21}$-$PAEMA_{300}$	1.50	0.2390	5.928	42 μL	30 μL



Figure S1. Schematic diagram of the custom-built device for the redox-initiated RAFT emulsion polymerization kinetics of AEMA (nitrogen flow through the tube during operation).

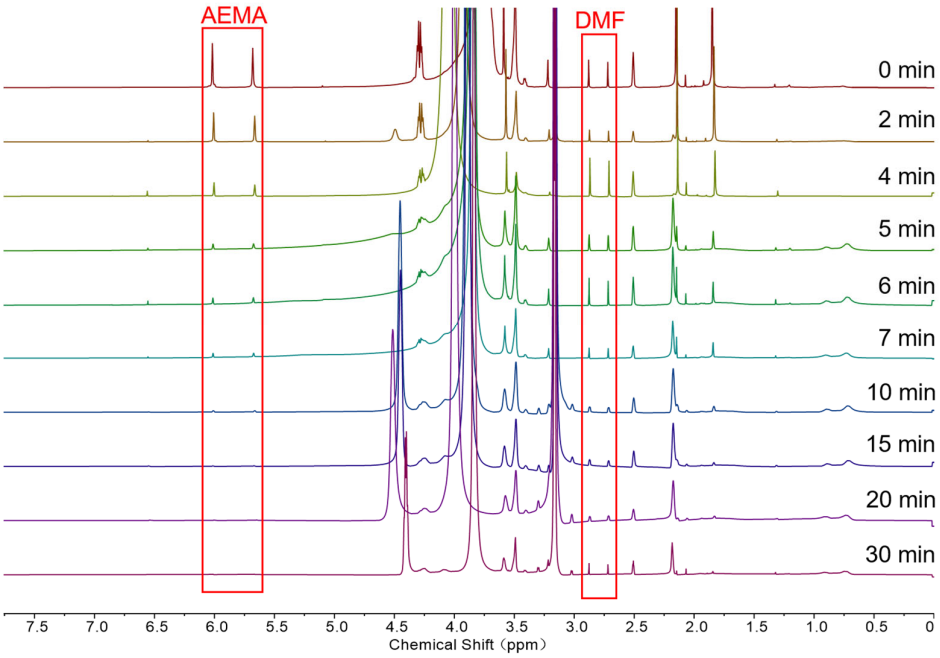

Figure S2. ^{1}H NMR spectra of aliquots withdrawn during RAFT emulsion polymerization of AEMA of 15% w/w, target composition of PPEGMA$_{12}$-PAEMA$_{100}$ at 50 °C. A small amount of DMF was used as the internal standard.

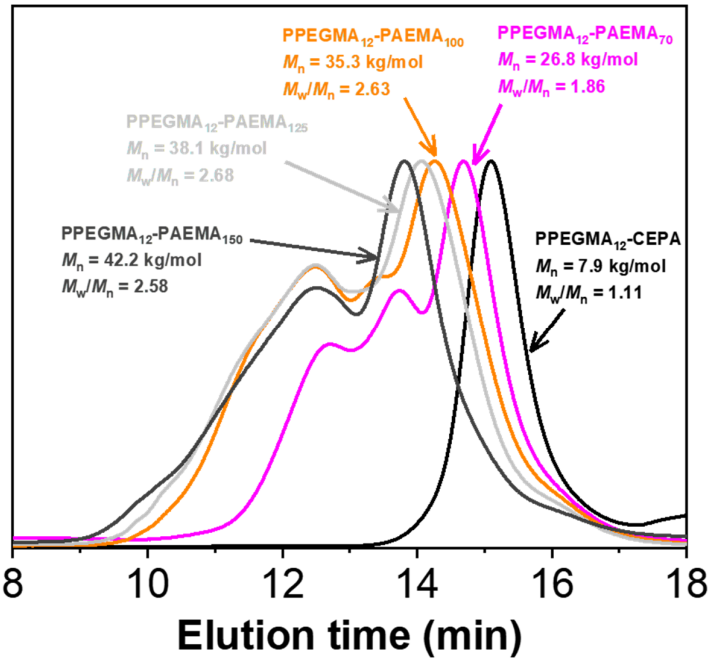

Figure S3. THF GPC traces of diblock copolymers formed by RAFT emulsion polymerization of AEMA (20% w/w).

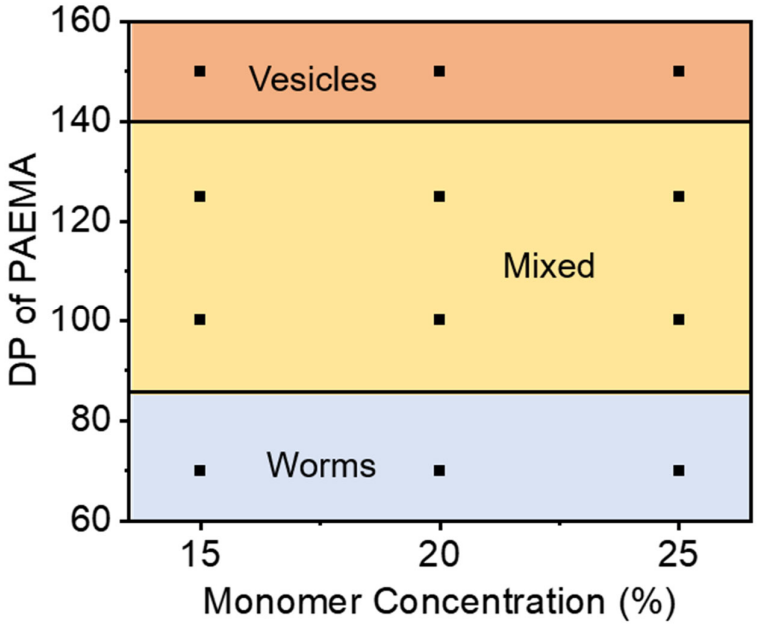

Figure S4. Morphological phase diagram constructed for PPEGMA$_{12}$-PAEMA$_m$ diblock copolymer assemblies prepared by RAFT emulsion polymerization of AEMA.

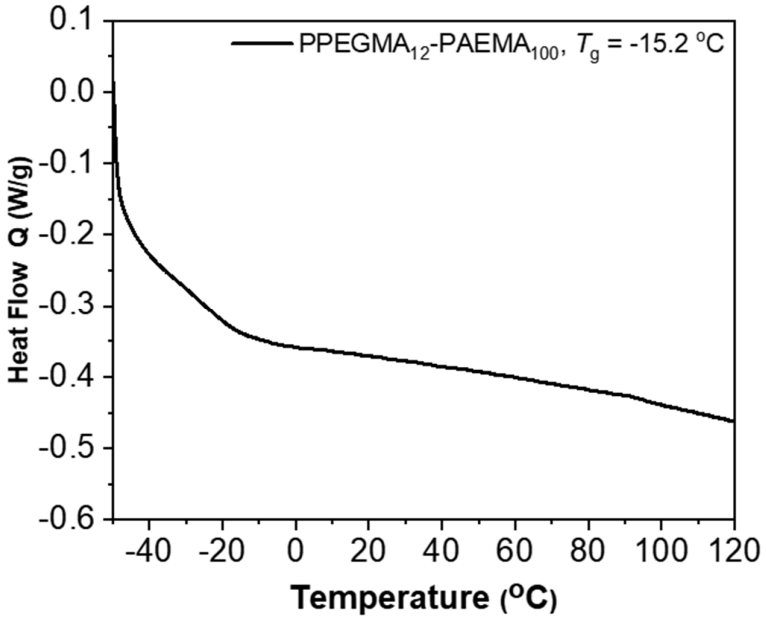

Figure S5. DSC curve of the block copolymer $PPEGMA_{12}$-$PAEMA_{100}$ obtained by RAFT emulsion polymerization of AEMA.

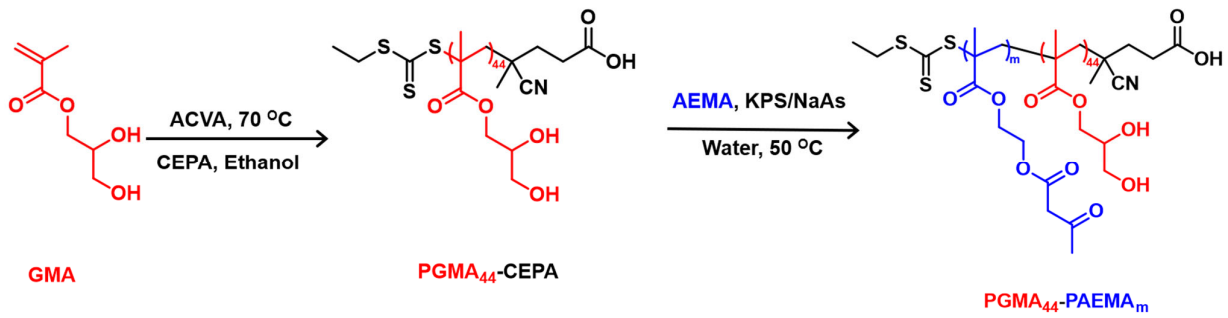

Figure S6. Synthesis of poly(glycerol monomethacrylate)-poly(2-(acetoacetoxy) ethyl methacrylate) ($PGMA_{44}$-$PAEMA_m$) diblock copolymer assemblies via redox-initiated RAFT-mediated emulsion polymerization.

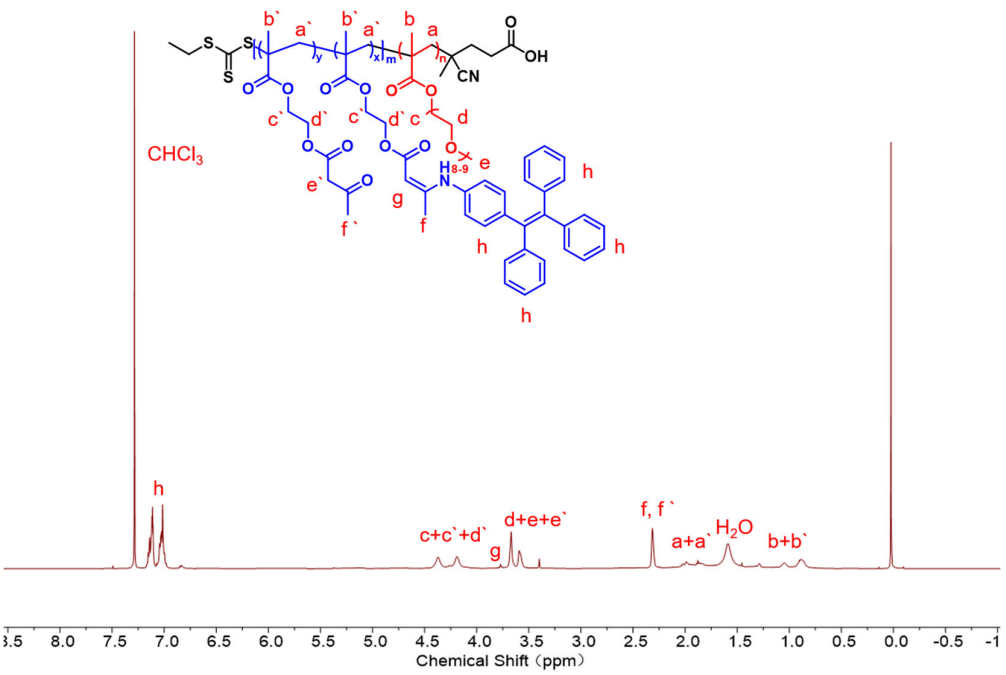

Figure S7. ^{1}H NMR spectra of AIE-polymer assemblies in $CDCl_3$, prepared via post-polymerization modification.

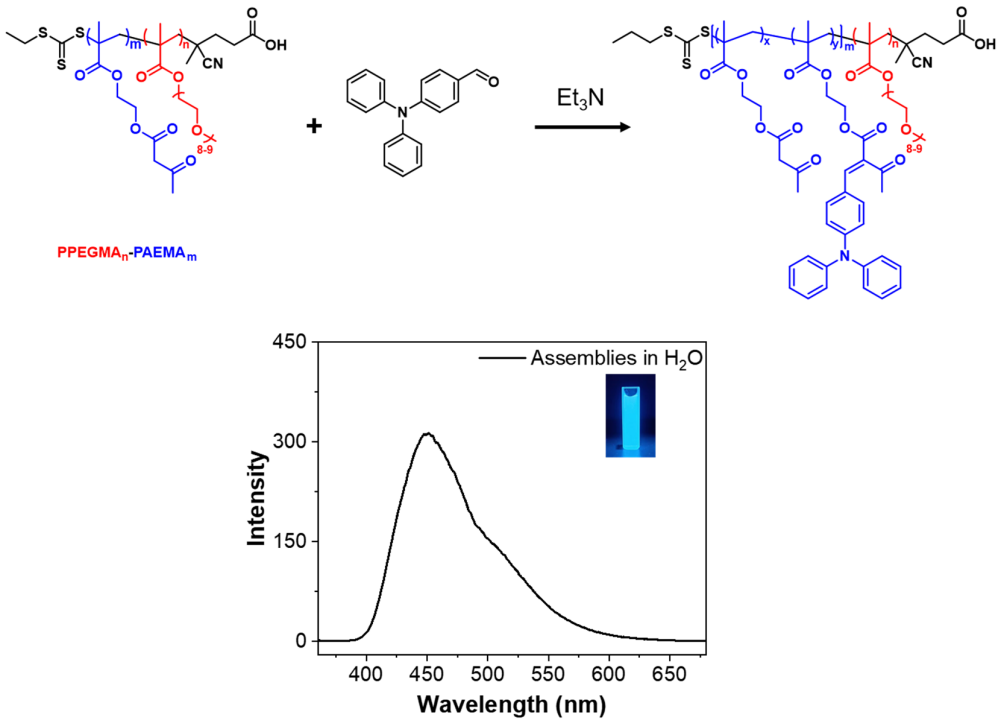

Figure S8. Schematic illustration of the preparation of AIE polymer assemblies via post-polymerization modification with aldehyde-based AIE molecules, along with the fluorescence emission spectra of the AIE polymer assemblies.