Supporting Information

Synthesis of low glass transition temperature worms comprising a poly(styrene-*stat-n*-butyl acrylate) core segment via polymerization-induced self-assembly in RAFT aqueous emulsion polymerization

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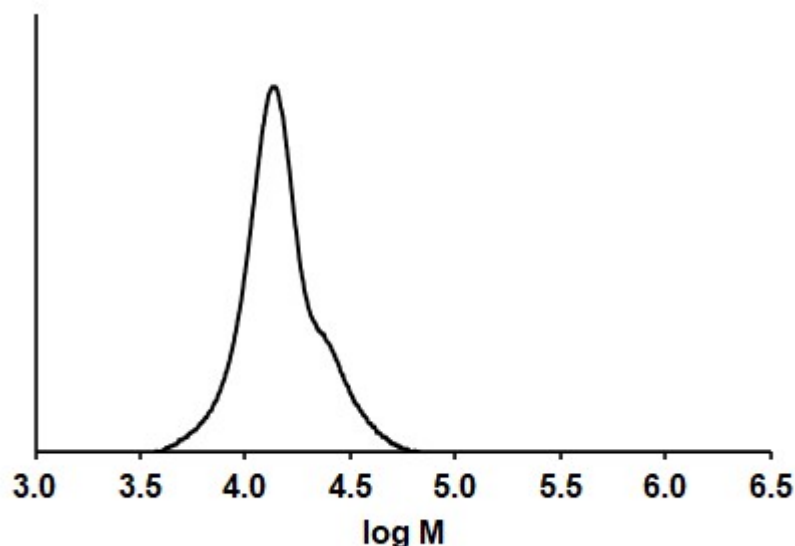
Fig. S1 Molecular weight distributions (w(log M) vs. log M) of P(AA-*stat*-PEGA)-TTC macroRAFT agent (M_n = 13,400 g/mol; $Đ$ = 1.20).
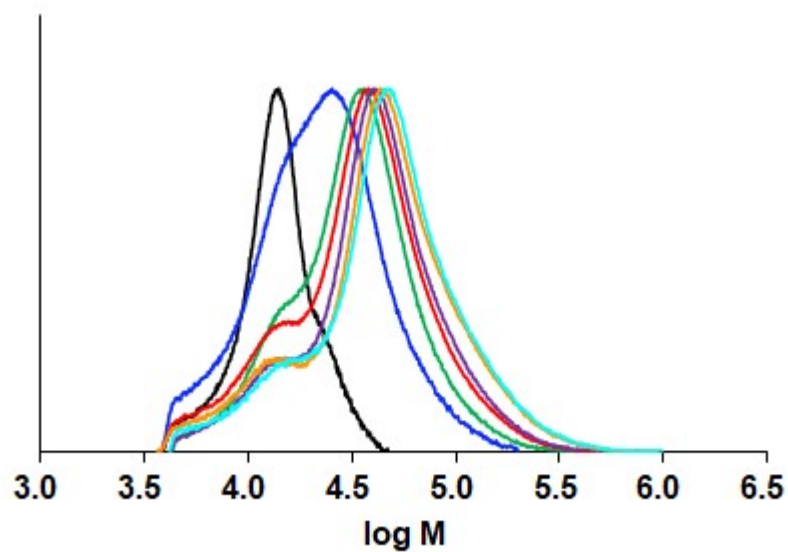
Fig. S2 Molecular weight distributions (w(log M) vs. log M) of RAFT aqueous emulsion polymerization of styrene and *n*BA in the presence of P(AA-*stat*-PEGA)-TTC macroRAFT agent with different [hydrophobic monomer]$_0$/[macroRAFT]$_0$ (macroRAFT agent, [hydrophobic monomer]$_0$/[macroRAFT]$_0$ = 50 (B-1), 100 (B-2), 130 (B-3), 150 (B-4), 170 (B-5), 200 (B-6) from left to right) (Table 2).

Table S1 Experimental conditions and results of RAFT aqueous emulsion polymerization of styrene and nBA in the presence of P(AA-*stat*-PEGA) macroRAFT agent at 80 °C for 4 h; pH 5, molar ratio AA/PEGA = 50/50, styrene/nBA = 70/30, $[\text{macroRAFT}]_0$ = 6.2 mmol/L, $[\text{NaHCO}_3]_0/[\text{ACPA}]_0$ = 3.5.

#	Crosslinker	$[\text{M}]_0/[\text{crosslinker}]_0/[\text{RAFT}]_0$	Conv.[a] (%)	$M_{n,th}$[b] (g/mol)	Solids content[c] (%)
Entries C-x and D-x: crosslinker added at t = 0 h					
C-1	PEGDA	100/1/1	73[a]	20,200[b]	12.6
C-2	PEGDA	100/2.5/1	98[a]	23,100[b]	12.7
D-1	EGDA	100/0.5/1	92	22,000	12.7
D-2	EGDA	100/1/1	89	22,800	12.5
D-3	EGDA	100/10/1	89	23,300	13.4
Entreis E-x and F-x: crosslinker added at t = 2 h					
E-1	PEGDA	100/1/1	69[a]	19,800[b]	12.6
E-2	PEGDA	100/10/1	100[a]	25,500[b]	13.7
F-1	EGDA	100/3/1	92	22,100	12.6
F-2	EGDA	100/5/1	93	23,100	12.9
F-3	EGDA	100/10/1	100	24,700	13.3

[a] Monomer conversion by gravimetry. Note that PEGDA was non-volatile and was excluded from calculation of monomer conversion determined by gravimetry.
[b] Theoretical $M_{n,th}$ calculated using monomer conversion obtained from gravimetry via eqn (S1).
[c] Solids content in wt% based on total weight.

The theoretical number-average molecular weight ($M_{n,th}$) was determined by eqn (S1):

$$M_{n,th} = M_{macroRAFT} + \frac{\left(X_{conv} \cdot [\text{styrene}]_0 \cdot M_S\right) + \left(X_{conv} \cdot [n\text{BA}]_0 \cdot M_{n\text{BA}}\right) + \left(X_{conv} \cdot [\text{EGDA}]_0 \cdot M_{\text{EGDA}}\right)}{[\text{macroRAFT}]_0} \tag{S1}$$

where $M_{macroRAFT}$, M_S, $M_{n\text{BA}}$, M_{EGDA} are the molar masses of macroRAFT agent, styrene, nBA, and EGDA, respectively, $[\text{macroRAFT}]_0$, $[\text{styrene}]_0$, $[n\text{BA}]_0$, $[\text{EGDA}]_0$ are the initial concentrations of macroRAFT agent, styrene, nBA, and EGDA respectively, and X_{conv} denotes total monomer conversion determined by gravimetry.

Table S2 Experimental conditions and results of RAFT aqueous emulsion polymerization of styrene and *n*BA in the presence of P(AA-*stat*-PEGA) macroRAFT agent at 80 °C, EGDA added at $t = 2$ h; pH 5, molar ratio AA/PEGA = 50/50, styrene/*n*BA = 20/80, EGDA/macroRAFT = 5/1, $[\text{macroRAFT}]_0 = 6.2$ mmol/L, $[\text{NaHCO}_3]_0/[\text{ACPA}]_0 = 3.5$.

#	DP	t (h)	Conv.[a] (%)	$M_{n,th}$[b] (g/mol)	Solids content[c] (%)
G-1	80	4	100	22,300	12.2
G-2	100	4	100	24,600	13.4
G-3	115	4	98	26,300	14.2
G-4	130	4	100	28,800	15.2
G-5	150	4	100	30,800	16.1
G-6	180	4	100	34,500	17.9
G-7	200	4	96	35,900	18.7
G-8	250	4	94	41,200	21.1
G-9	300	4	93	46,600	23.5

[a] Monomer conversion by gravimetry.
[b] Theoretical $M_{n,th}$ calculated using monomer conversion obtained from gravimetry via eqn (S1).
[c] Solids content in wt% based on total weight.
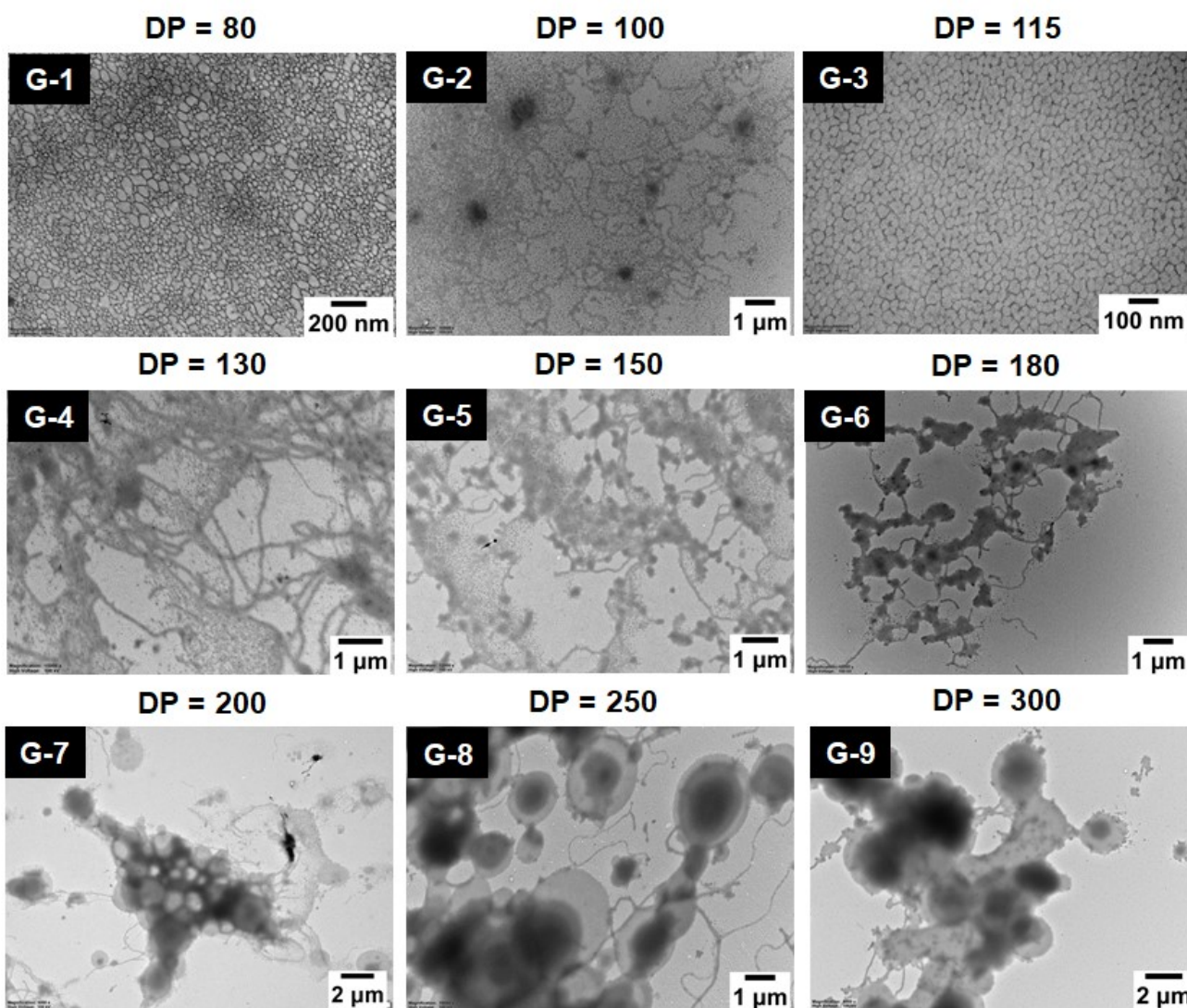
Fig. S3 TEM images of nanoparticles synthesized via RAFT aqueous emulsion polymerization of styrene and nBA ([styrene]$_0$/[nBA]$_0$ = 20/80, solids content varied from 12.2% to 23.5%) in the presence of P(AA-*stat*-PEGA)-TTC macroRAFT agent at pH 5 with EGDA ([EGDA]$_0$/[macroRAFT]$_0$ = 5/1) after 2 h of the polymerization with different [hydrophobic monomer]$_0$/[macroRAFT]$_0$ ([hydrophobic monomer]$_0$/[macroRAFT]$_0$ = 80 (G-1), 100 (G-2), 115 (G-3), 130 (G-4), 150 (G-5), 180 (G-6), 200 (G-7), 250 (G-8), 300 (G-9)). Scale bars: G-1 = 200 nm, G-2 = 1 µm, G-3 = 100 nm, G-4 = 1 µm, G-5 = 1 µm, G-6 = 1 µm, G-7 = 2 µm, G-8 = 1 µm, G-9 = 2 µm.

Table S3 Experimental conditions and results of RAFT aqueous emulsion polymerization of styrene and nBA in the presence of P(AA-$stat$-PEGA) macroRAFT agent at 80 °C for 4 h, EGDA added at t = 2 h; pH 5, molar ratio AA/PEGA = 50/50, styrene/nBA = 20/80, EGDA/macroRAFT = 5/1, [macroRAFT]$_0$ = 6.2 mmol/L, [NaHCO$_3$]$_0$/[ACPA]$_0$ = 3.5.

#	DP	t (h)	Conv.[a] (%)	$M_{n,th}$[b] (g/mol)	Solids content[c] (%)
H-1	130	4	100	28,800	15.2
H-2	130	4	100	28,300	24.7
H-3	130	4	91	26,800	32.7

[a] Monomer conversion by gravimetry.
[b] Theoretical $M_{n,th}$ calculated using monomer conversion obtained from gravimetry via eqn (S1).
[c] Solids content in wt% based on total weight.
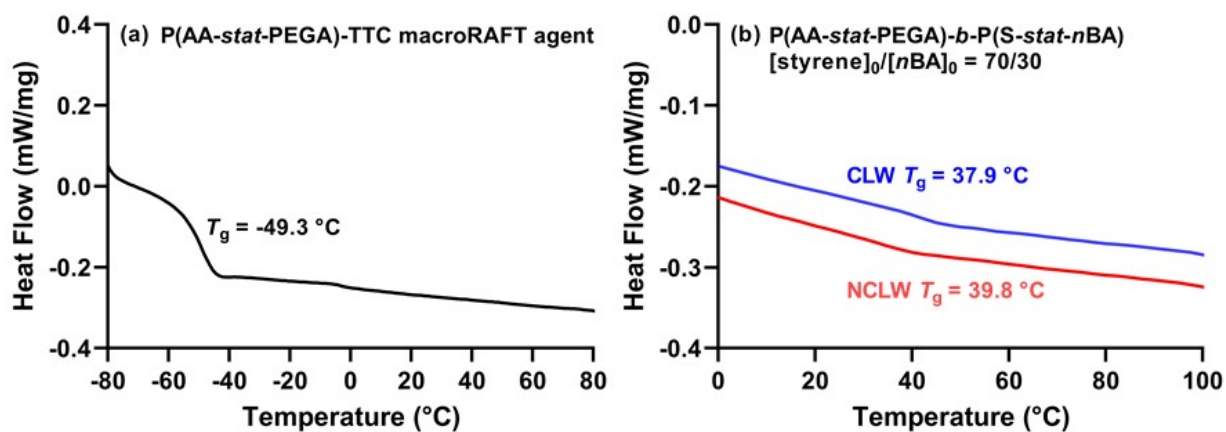
Fig. S4 DSC traces of (a) P(AA-*stat*-PEGA)-TTC maroRAFT agent, (b) P(AA-*stat*-PEGA)-*b*-P(S-*stat*-*n*BA) non-crosslinked worms (NCLW) and crosslinked worms (CLW) ([styrene]$_0$/[nBA]$_0$ = 70/30).