Supporting Information for RAFT Dispersion Polymerization in Non-Polar Solvents: Facile Production of Block Copolymer Spheres, Worms and Vesicles in *n*-Alkanes

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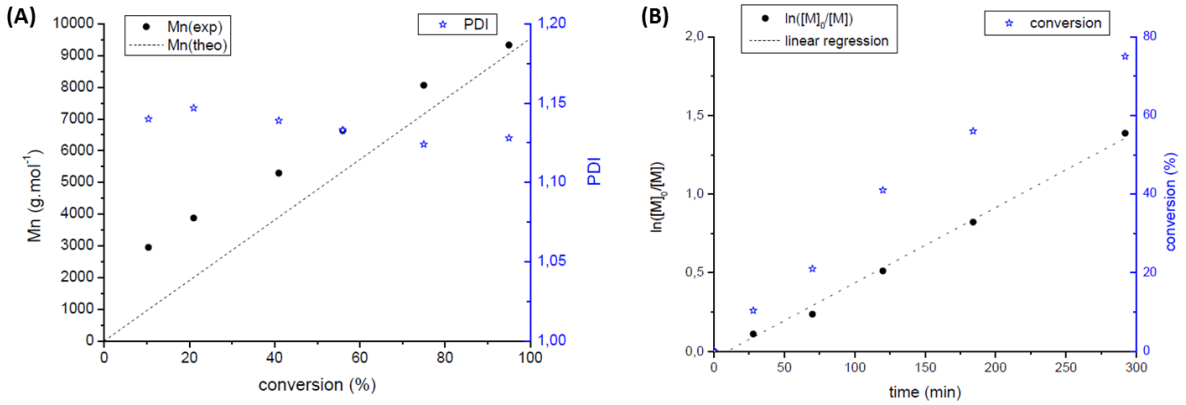

Figure S1. RAFT polymerization of LMA in toluene at 70°C and 50 wt. % solids using CPDB CTA. The targeted composition was $PLMA_{38}$ and the CTA/initiator molar ratio was 5.0. (A) evolution of M_n and M_w/M_n with monomer conversion, as judged by THF GPC (vs. poly(methyl methacrylate) calibration standards); (B) Conversion vs. time data calculated from ^{1}H NMR spectra.

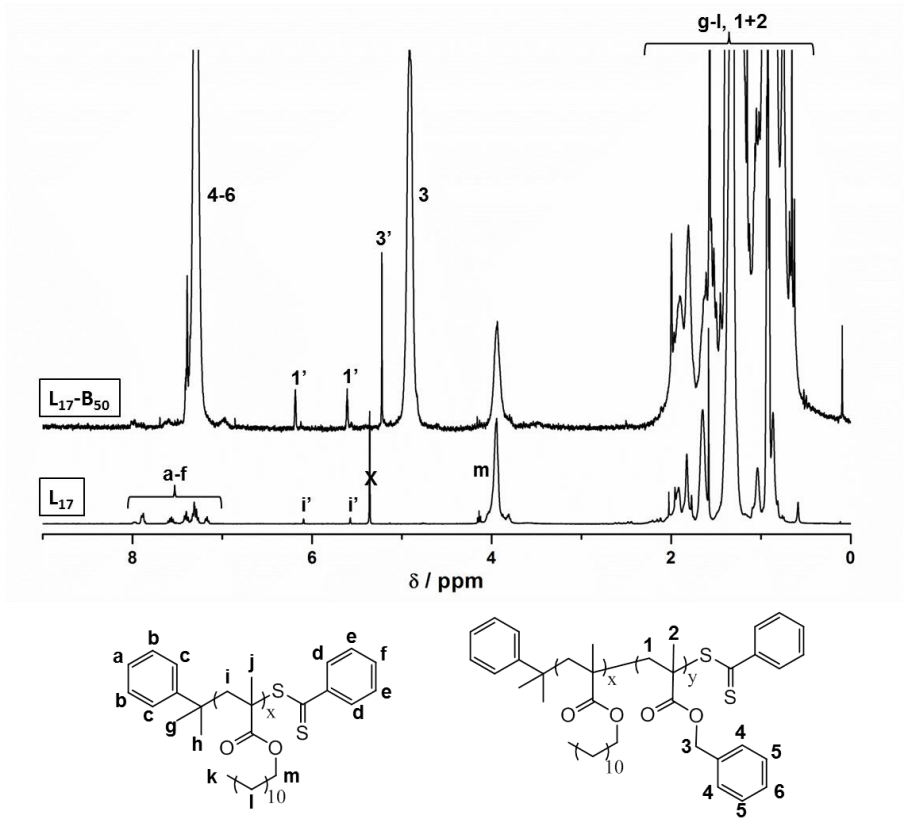

Figure S2. Assigned ^{1}H NMR spectra obtained for the $PLMA_{17}$ macro-CTA (in CD_2Cl_2) and a $PLMA_{17}$-$PBzMA_{50}$ diblock copolymer (in $CDCl_3$).

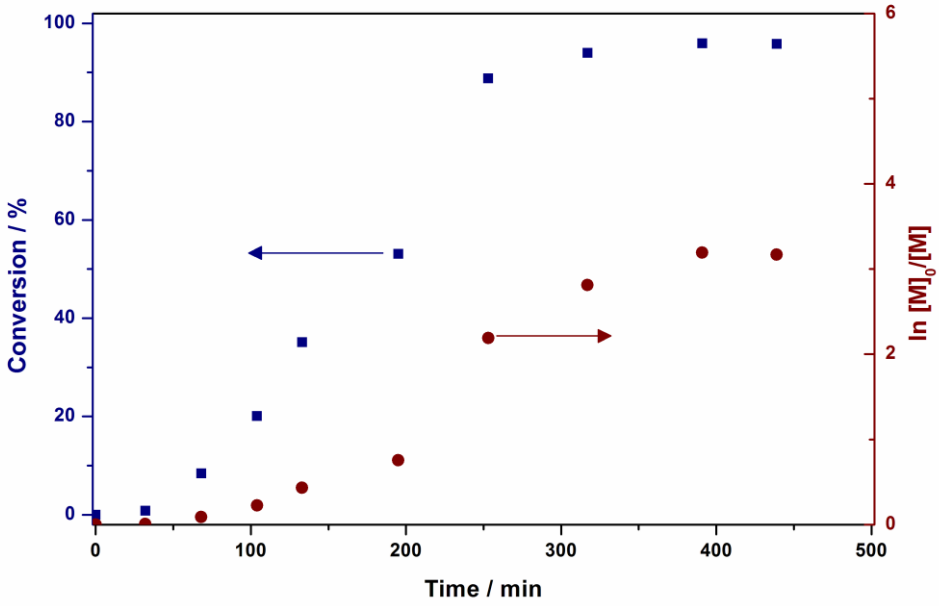

Figure S3. Conversion vs. time curve and corresponding semi-logarithmic plot obtained for the polymerization of BzMA at 90°C using a $PLMA_{17}$ macro-CTA under RAFT dispersion polymerization conditions in *n*-heptane at 15 wt. % solids. Conditions: target DP for the PBzMA block = 300; macro-CTA/initiator molar ratio = 2.0.

Table S1. Summary of monomer conversions, calculated degrees of polymerization and GPC molecular weights for PLMA macro-CTAs synthesized by RAFT solution polymerization of LMA in toluene at 70°C using AIBN. Conditions: $[LMA]_0$ = 50 wt. %, CTA/AIBN molar ratio = 5.0.

Targeted degree of polymerization	CTA type	NMR conversion	Mean DP (^{1}H NMR)	THF GPC		
				M_n / g mol^{-1}	M_w / g mol^{-1}	M_w/M_n
$PLMA_{10}$	CDB	85	17	4 900	5 900	1.20
$PLMA_{40}$	CDB	74	37	9 800	12 000	1.23
$PLMA_{60}$	CDB	73	47	12 800	16 100	1.26
$PLMA_{38}$	CPDB	85	39	8 900	9 900	1.11
$PLMA_{35}$	PETTC	95	45	9 100	10 300	1.13
$PLMA_{70}$	PETTC	74	75	13 000	15 000	1.16

Table S2. Summary of monomer conversions, particle diameters and molecular weights obtained for $PLMA_{17}$-$PBzMA_x$ syntheses conducted by RAFT dispersion polymerization of BzMA in *n*-heptane at 90°C using T21s initiator (macro-CTA/initiator molar ratio = 2.0) for at least 18 h at 12.5 to 25.0 % solids.

Solids	Target composition	BzMA % conversion	Actual PBzMA DP	GPC		DLS		TEM morphology
				M_n	M_w/M_n	diameter	PDI	
12.5	$PLMA_{17}$-$PBzMA_{200}$	98	196	51 600	1.18	162	0.038	Vesicles
	$PLMA_{17}$-$PBzMA_{150}$	97	146	43 800	1.15	158	0.031	Vesicles
	$PLMA_{17}$-$PBzMA_{100}$	97	97	25 600	1.29	153	0.055	Vesicles
	$PLMA_{17}$-$PBzMA_{75}$	96	72	19 400	1.30	131	0.060	Vesicles and worms
	$PLMA_{17}$-$PBzMA_{63}$	98	62	18 400	1.39	91	0.067	Vesicles and worms
	PLM_{17}-$PBzMA_{50}$	96	48	14 800	1.32	98	0.378	Worms and spheres
	$PLMA_{17}$-$PBzMA_{38}$	97	37	13 400	1.34	30	0.020	Spheres
	$PLMA_{17}$-$PBzMA_{25}$	91	23	9 800	1.25	27	0.051	Spheres
15.0	$PLMA_{17}$-$PBzMA_{300}$	98	294	57 100	1.18	182	0.050	Vesicles
	$PLMA_{17}$-$PBzMA_{250}$	96	240	50 600	1.24	171	0.032	Vesicles
	$PLMA_{17}$-$PBzMA_{200}$	96	192	50 300	1.18	173	0.051	Vesicles
	$PLMA_{17}$-$PBzMA_{150}$	97	146	49 300	1.20	164	0.040	Vesicles
	$PLMA_{17}$-$PBzMA_{100}$	98	98	38 800	1.14	161	0.045	Vesicles
	$PLMA_{17}$-$PBzMA_{75}$	98	74	23 200	1.30	105	0.056	Vesicles and worms
	$PLMA_{17}$-$PBzMA_{63}$	98	62	18 600	1.40	107	0.066	Vesicles and worms
	$PLMA_{17}$-$PBzMA_{50}$	97	49	20 600	1.32	205	0.325	Vesicles and worms
	$PLMA_{17}$-$PBzMA_{25}$	96	24	10 600	1.41	48	0.278	Spheres
17.5	$PLMA_{17}$-$PBzMA_{125}$	98	123	30 800	1.47	166	0.032	Vesicles
	$PLMA_{17}$-$PBzMA_{88}$	98	86	22 500	1.34	179	0.091	Vesicles
	$PLMA_{17}$-$PBzMA_{75}$	98	74	19 500	1.41	168	0.243	Vesicles and worms
	$PLMA_{17}$-$PBzMA_{63}$	98	62	19 000	1.37	390	0.604	Worms
	$PLMA_{17}$-$PBzMA_{50}$	97	49	15 500	1.35	44	0.084	Worms and spheres
	$PLMA_{17}$-$PBzMA_{38}$	99	38	13 600	1.28	62	0.134	Worms and spheres
20.0	$PLMA_{17}$-$PBzMA_{300}$	98	294	71 500	1.35	188	0.015	Vesicles
	$PLMA_{17}$-$PBzMA_{250}$	98	245	64 700	1.26	217	0.176	Vesicles
	$PLMA_{17}$-$PBzMA_{200}$	98	196	59 700	1.22	191	0.099	Vesicles
	$PLMA_{17}$-$PBzMA_{150}$	98	147	47 300	1.25	179	0.042	Vesicles
	$PLMA_{17}$-$PBzMA_{100}$	98	98	28 600	1.29	153	0.075	Vesicles
	$PLMA_{17}$-$PBzMA_{75}$	99	74	22 800	1.32	476	0.460	Vesicles and worms
	$PLMA_{17}$-$PBzMA_{63}$	98	62	18 100	1.36	216	0.307	Worms
	$PLMA_{17}$-$PBzMA_{50}$	98	49	14 000	1.35	136	0.224	Worms
	$PLMA_{17}$-$PBzMA_{38}$	97	37	13 300	1.33	29	0.017	Spheres
	$PLMA_{17}$-$PBzMA_{25}$	96	24	10 300	1.32	26	0.003	Spheres
21.2	$PLMA_{17}$-$PBzMA_{50}$	98	49	13 700	1.30	53	0.128	Worms
22.5	$PLMA_{17}$-$PBzMA_{175}$	99	173	48 100	1.17	192	0.023	Vesicles
	$PLMA_{17}$-$PBzMA_{125}$	99	124	29 400	1.33	196	0.100	Vesicles
	$PLMA_{17}$-$PBzMA_{88}$	99	87	23 700	1.58	178	0.133	Vesicles
	$PLMA_{17}$-$PBzMA_{63}$	99	62	17 400	1.42	680	0.501	Worms
	$PLMA_{17}$-$PBzMA_{50}$	98	49	15 000	1.31	52	0.140	Worms and spheres
	$PLMA_{17}$-$PBzMA_{38}$	99	38	12 900	1.38	122	0.355	Worms and spheres
	$PLMA_{17}$-$PBzMA_{25}$	95	24	10 500	1.29	21	0.041	Spheres
23.8	$PLMA_{17}$-$PBzMA_{50}$	99	50	13 300	1.32	68	0.134	Worms and spheres
	$PLMA_{17}$-$PBzMA_{38}$	97	37	12 700	1.31	27	0.015	Spheres
	$PLMA_{17}$-$PBzMA_{25}$	97	24	10 500	1.30	21	0.034	Spheres
25.0	$PLMA_{17}$-$PBzMA_{300}$	99	297	62 700	1.34	220	0.097	Vesicles
	$PLMA_{17}$-$PBzMA_{250}$	98	245	54 500	1.18	217	0.093	Vesicles
	$PLMA_{17}$-$PBzMA_{200}$	99	198	46 400	1.17	216	0.150	Vesicles
	$PLMA_{17}$-$PBzMA_{150}$	99	149	39 700	1.15	201	0.078	Vesicles
	$PLMA_{17}$-$PBzMA_{100}$	98	98	28 800	1.16	200	0.122	Vesicles
	$PLMA_{17}$-$PBzMA_{75}$	99	74	26 400	1.15	749	0.704	Vesicles and worms
	$PLMA_{17}$-$PBzMA_{63}$	98	62	15 900	1.34	223	0.362	Worms
	$PLMA_{17}$-$PBzMA_{50}$	98	49	15 800	1.37	85	0.139	Worms
	$PLMA_{17}$-$PBzMA_{38}$	98	37	12 200	1.27	31	0.186	Spheres
	$PLMA_{17}$-$PBzMA_{25}$	99	25	10 400	1.30	32	0.046	Spheres

Table S3. Summary of monomer conversions, particle diameters and molecular weights obtained for $PLMA_{17}$-$PBzMA_x$ syntheses conducted by RAFT dispersion polymerization of BzMA in *n*-heptane at 90°C using T21s initiator (macro-CTA/initiator molar ratio = 5.0) for at least 18 h at 15.0 to 17.5 % solids.

Solids	Target composition	BzMA % conversion	Actual PBzMA DP	GPC		DLS		TEM morphology
				M_n	M_w/M_n	diameter	PDI	
15.0	$PLMA_{17}$-$PBzMA_{175}$	97	170	33 500	1.33	176	0.032	Vesicles
	$PLMA_{17}$-$PBzMA_{125}$	97	121	27 800	1.27	180	0.060	Vesicles
	$PLMA_{17}$-$PBzMA_{75}$	93	70	20 600	1.33	191	0.134	Vesicles
	$PLMA_{17}$-$PBzMA_{35}$	94	33	11 700	1.22	27	0.025	Spheres
17.5	$PLMA_{17}$-$PBzMA_{175}$	96	168	45 100	1.33	179	0.020	Vesicles
	$PLMA_{17}$-$PBzMA_{25}$	89	22	9 300	1.20	21	0.032	Spheres

Table S4. Summary of monomer conversions, particle diameters and molecular weights obtained for $PLMA_x$-$PBzMA_y$ syntheses conducted by RAFT dispersion polymerization in *n*-heptane at 90°C using T21s initiator (macro-CTA/initiator molar ratio = 2.0) for at least 18 h at 15 % solids.

Target composition	BzMA % conversion	Actual PBzMA DP	GPC		DLS		TEM morphology
			M_n	M_w/M_n	diameter	PDI	
$PLMA_{37}$-$PBzMA_{900}$	97	873	181 500	1.69	139	0.041	Spheres
$PLMA_{37}$-$PBzMA_{700}$	98	686	170 100	1.51	117	0.008	Spheres
$PLMA_{37}$-$PBzMA_{500}$	93	465	79 300	1.72	88	0.014	Spheres
$PLMA_{37}$-$PBzMA_{300}$	98	294	65 300	1.61	70	0.016	Spheres
$PLMA_{37}$-$PBzMA_{100}$	97	97	29 700	1.34	41	0.008	Spheres
$PLMA_{39}$-$PBzMA_{300}$	97	291	70 800	1.16	63	0.007	Spheres
$PLMA_{39}$-$PBzMA_{150}$	96	144	43 100	1.48	49	0.024	Spheres
$PLMA_{45}$-$PBzMA_{300}$	97	291	42 200	1.34	61	0.018	Spheres
$PLMA_{45}$-$PBzMA_{150}$	97	146	25 800	1.28	43	0.018	Spheres
$PLMA_{47}$-$PBzMA_{900}$	98	882	192 300	1.76	119	0.026	Spheres
$PLMA_{47}$-$PBzMA_{700}$	97	679	202 900	1.63	108	0.025	Spheres
$PLMA_{47}$-$PBzMA_{300}$	98	294	99 000	1.37	70	0.018	Spheres
$PLMA_{47}$-$PBzMA_{100}$	98	98	32 700	1.52	45	0.011	Spheres
$PLMA_{75}$-$PBzMA_{300}$	98	294	38 400	1.61	53	0.037	Spheres