SUPPORTING INFORMATION:

Self-assembly of poly(lauryl methacrylate)-*b*-poly(benzyl methacrylate) nano-objects synthesised by ATRP and their temperature-responsive dispersion properties

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Calculation of macroinitiator and copolymer compositions from ^{1}H NMR data

The structure for the macroinitator used is shown in Fig. S1. The macroinitiaor is abbreviated as L_x for the purposes of the following calculation. Equation S1 was used to calculate the degree of polymerisation (x).

$$x = \frac{1}{6}\left(\left(\frac{A_h + A_c}{A_a}\right) - 2\right) \qquad \text{(S1)}$$

For the above equations A_h, A_c and A_a are the integrals of the signals from the **h**, **c** and **a** protons, respectively.

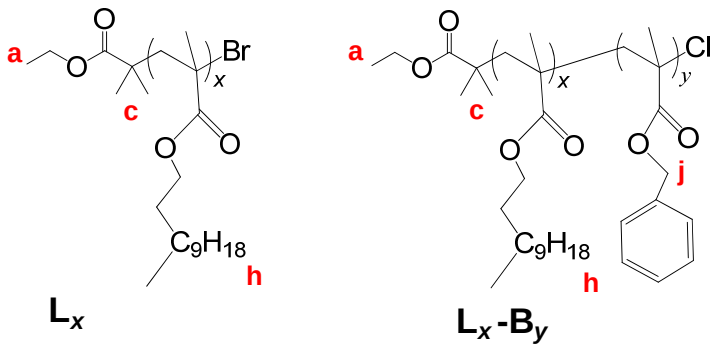

Fig. S1. Structures and assignments for calculating x and y for the macroinitiator and diblock copolymers used in this study.

The following equation was used to determine the number of BzMA repeat units (y) in the L_x-B_y copolymers (Fig. S1) using the ^{1}H NMR data shown in Fig. 1.

$$y = (9x + 3)\left(\frac{A_j}{A_h + A_c}\right) \qquad \text{(S2)}$$

For equation (S2), A_j is the integral of the signal from the **j** protons and a value for *x* of 14.0 was used.

Calculation of N_{agg} and average separation between PLMA chains at the sphere surface

To calculate the aggregation number (N_{agg}) from the number-average diameter of the spheres determined from TEM (d_{TEM}) it was assumed that the latter corresponded to pure PBzMA without residual solvent. The latter assumption is supported by the literature[1]. The procedure involved calculating the mass of one PBzMA chain (m_{PBzMA}) and also the mass of an average sphere (m_{sphere}). These two values were then used to calculate N_{agg}. The value for m_{PBzMA} was calculated using

$$m_{PBzMA} = \frac{MW_{PBzMA}}{N_A} \qquad \text{(S3)}$$

where MW_{PBzMA} is molecular weight of the PBzMA segment (34 x 176 g/mol = 5984 g/mol) and N_A is Avogadro's number. These values gave m_{PBzMA} = 1.0 x 10^{-20} g. The value for m_{sphere} was calculated using

$$m_{sphere} = \frac{\pi \rho_{PBzMA} d_{TEM}^3}{6} \qquad \text{(S4)}$$

where ρ_{PBzMA} is the density of PBzMA. The latter was taken as[2] 1.18 g/cm^3. Using d_{TEM} = 20.5 nm a value of m_{sphere} = 5.3 x 10^{-18} g was calculated. These data enabled the value for N_{agg} (= m_{sphere} / m_{PBzMA}) to be calculated as 530.

The average separation of chains at the sphere surface was estimated using N_{agg} and the average surface area of the spheres (A_{sphere}). A value of 1.3 x 10^{-15} m^2 for the latter was calculated using $A_{sphere} = \pi d_{TEM}^2$. The area per chain at the surface (A_{chain}) was then determined using A_{chain} = (A_{sphere} / N_{agg}) = 2.5 nm^2. The average separation between the chains at the surface would be ~ 1.6 nm assuming a cubic lattice at the surface.

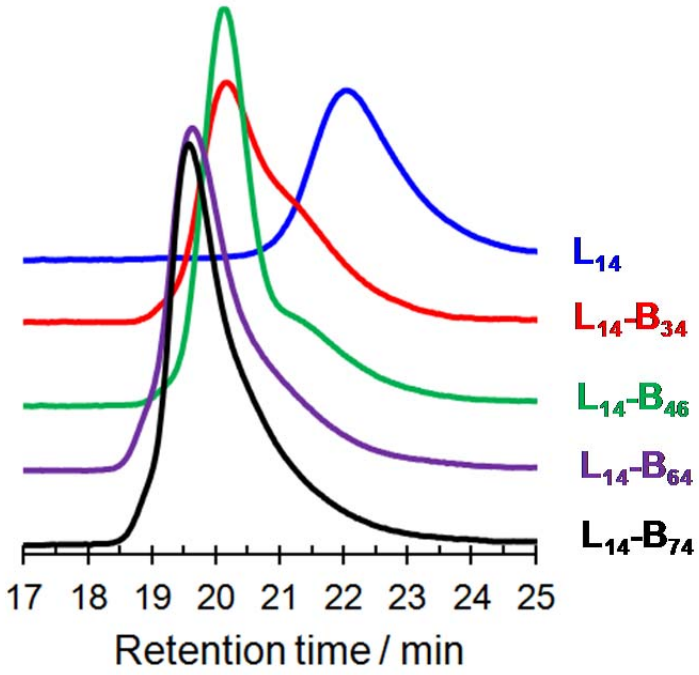

Fig. S2 GPC chromatograms for the macroinitiator (L_{14}) and the diblock copolymers (L_{14}-B_{34} – L_{14}-B_{74}). The chromatograms were obtained using THF eluent and polystyrene standards.

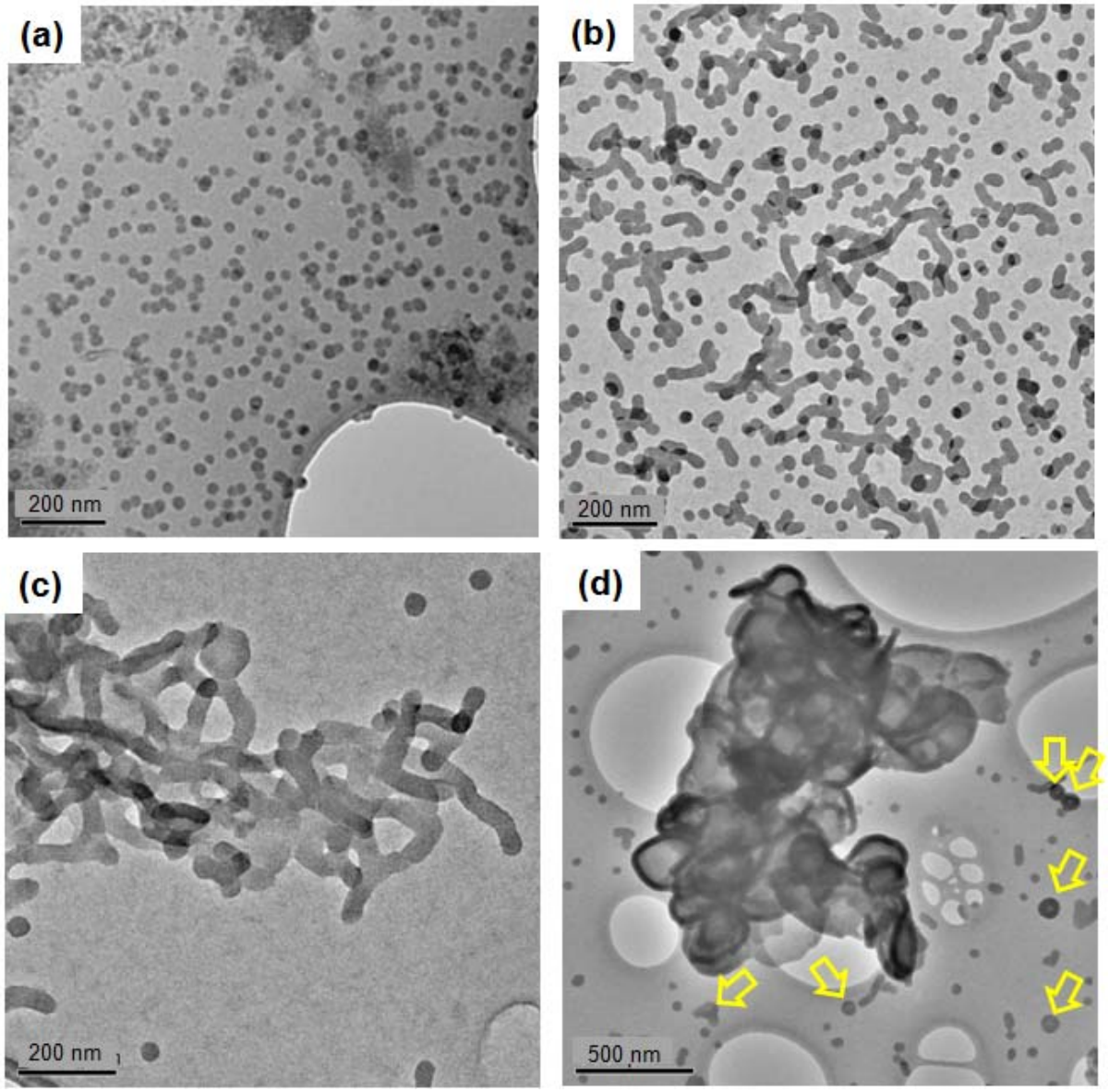

Fig. S3 Low magnification TEM images of diblock copolymer nano-objects deposited from *n*-dodecane dispersions containing (a) L_{14}-B_{34}, (b) L_{14}-B_{46}, (c) L_{14}-B_{64} and (d) L_{14}-B_{74}. The samples were stained with ruthenium tetra-oxide. The arrows in (d) highlight small vesicles.

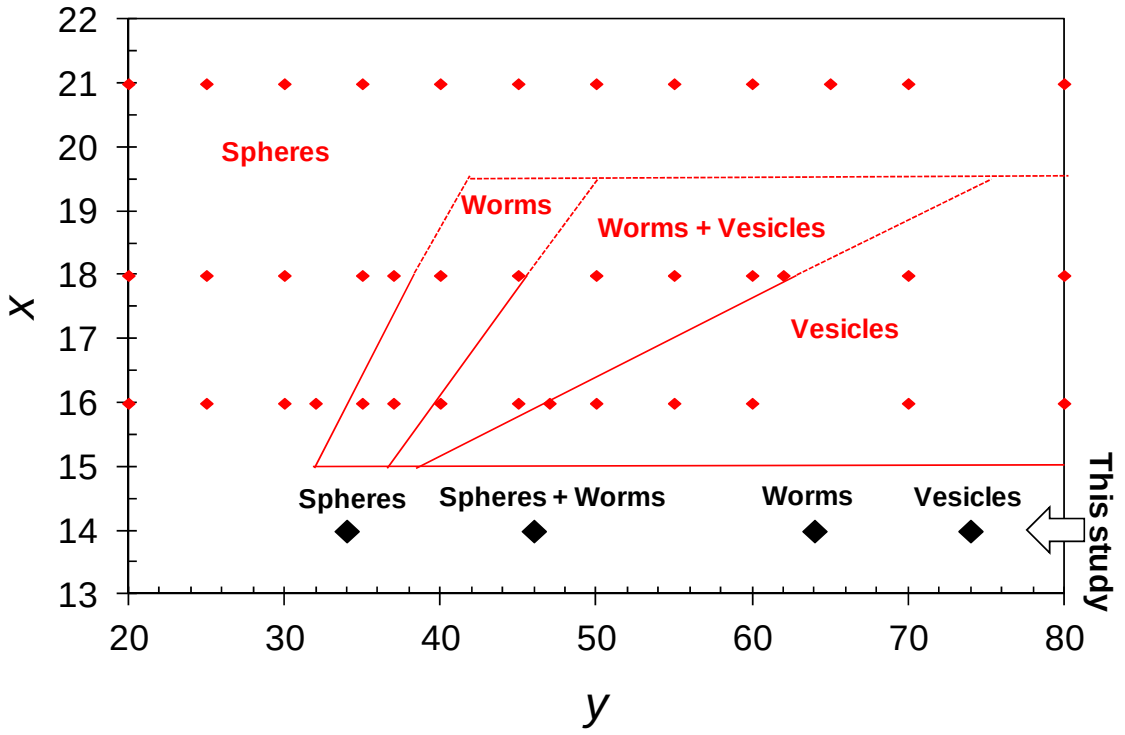

Fig. S4 Phase diagram comparing ATRP-based $PLMA_x$-$PBzMA_y$ diblock copolymer nano-objects from the present study (black diamonds and labels) with those prepared by non-aqueous RAFT dispersion polymerisation from Ref. 3 (red diamonds and labels).

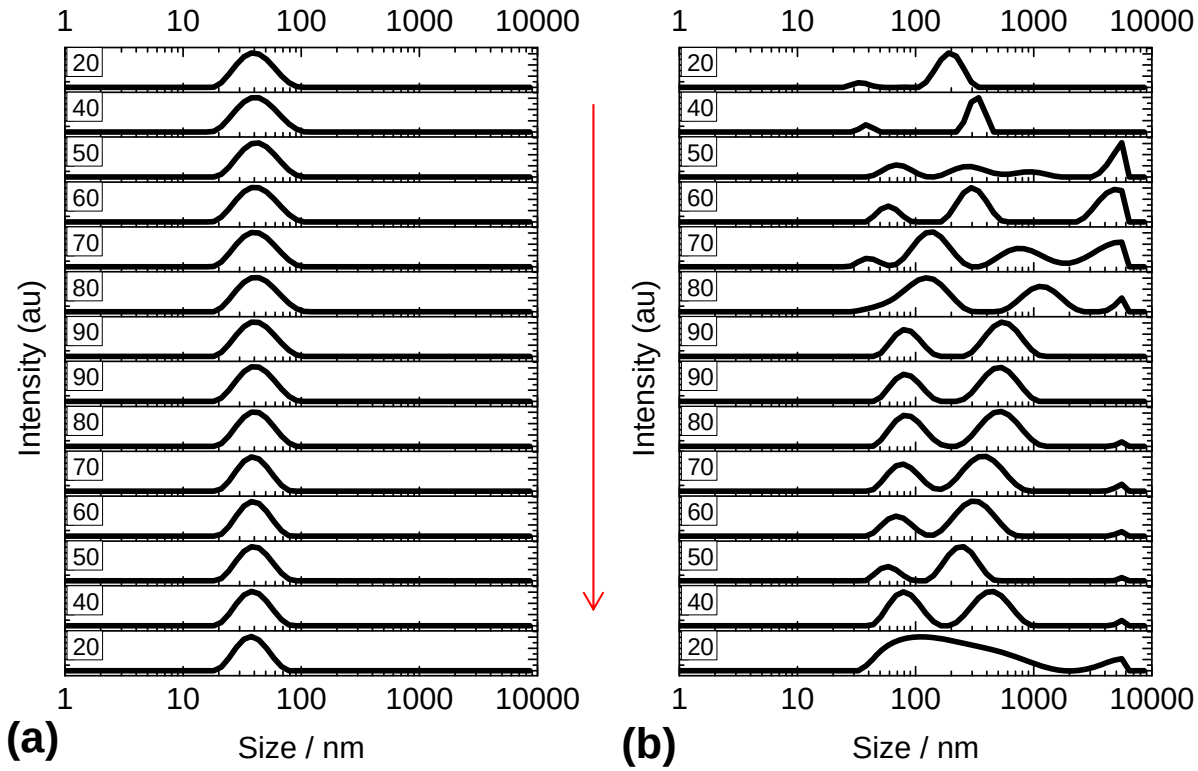

Fig. S5 Dynamic light scattering size distributions for (a) L_{14}-B_{34} spheres and (b) L_{14}-B_{64} worms. The temperatures are shown (^{o}C). The direction of the temperature ramp is shown with the arrow. The d_z and PDI data are shown in Fig. 4.

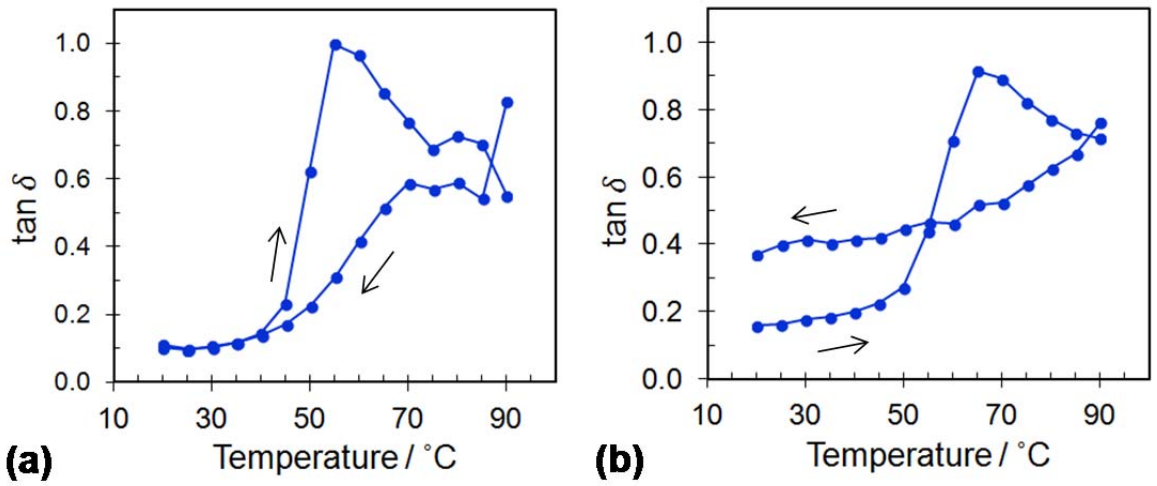

Fig. S6. Variation of tan δ (= G" / G', where G" and G' are the loss and storage modulus, respectively) with temperature for (a) L_{14}-B_{46} and (b) L_{14}-B_{64} dispersed in *n*-dodecane (20 % w/w). The measurements started at 20 ^{o}C.

References

1. M. J. Derry, L. A. Fielding, N. J. Warren, C. J. Mable, A. J. Smith, O. O. Mykhaylyk, and S. P. Armes. *Chem Sci* 2016.
2. *www.sigmaaldrich.com Accessed November 2, 2016*.
3. L. A. Fielding, J. A. Lane, M. J. Derry, O. O. Mykhaylyk, and S. P. Armes. *J Am Chem Soc* 2014, **136**, 5790-5798.