

# Polymer fullerene solution phase behaviour and film formation pathways

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## S1 Sample Concentrations

wt% PS	wt% C <sub>60</sub>	C <sub>60</sub> loading	State
0.00	0.26	100.00	S
0.00	0.32	100.00	P
0.00	0.32	100.00	P
0.00	0.30	100.00	P
0.00	0.30	100.00	P
0.00	0.29	100.00	P
0.00	0.28	100.00	P
0.00	0.27	100.00	S
0.12	0.25	67.57	S
0.13	0.32	71.64	P
0.17	0.29	62.86	P
0.20	0.33	61.96	P
0.22	0.28	56.25	P
0.24	0.25	51.95	P
0.29	0.28	49.47	P
0.29	0.22	42.86	S
0.29	0.26	47.31	P
0.29	0.26	47.31	P
0.30	0.11	26.98	S
0.31	0.23	43.21	S
0.52	0.19	27.12	S
0.57	0.15	20.68	S
0.59	0.15	20.54	S
0.60	0.27	31.18	P
0.60	0.25	29.57	P
0.60	0.11	14.81	S
0.61	0.21	25.31	S
0.61	0.26	29.77	P
0.94	0.20	17.86	S
0.94	0.27	22.46	P
0.98	0.10	9.48	S
1.00	0.26	21.00	P
1.00	0.26	20.42	P
1.00	0.05	5.05	S
1.01	0.10	8.76	S
1.02	0.25	19.42	P
1.48	0.15	9.22	S
1.57	0.17	9.72	S
1.63	0.15	8.38	S
1.95	0.10	4.93	S
1.96	0.18	8.44	P
1.97	0.19	8.76	P
2.34	0.12	5.02	S
2.48	0.26	9.63	P
2.79	0.16	5.55	P
3.97	0.21	4.99	P
4.13	0.05	1.10	S
4.19	0.12	2.78	S
4.89	0.09	1.90	S
4.97	0.05	0.93	S

Table S1: Summary of PS/C<sub>60</sub>/toluene mixtures investigated. All concentrations ( $c_i$ ) in the system are reported by the ratio of the mass of component  $i$  to the total mass of the solution (mass fraction of total ternary mass), mass fraction of C<sub>60</sub> and whether the system appeared stable (S) or precipitated (P) after two days of stirring.

## S2 Fullerene Clusters

The relationship between PS addition and C<sub>60</sub> concentration at which aggregation occurs is found to be initially linear. The gradient of this linear miscibility drop is tentatively modelled by a simple scaling model:

$$V_{free} = V_{total} - \alpha \left( \frac{4\pi R_g^3 N}{3} \right) \quad (1)$$

where the free volume ( $V_{free}$ ), available for C<sub>60</sub>, is calculated by subtracting the volume occupied by the polymer ( $V_{occ}$ ) from the total volume ( $V_{total}$ ).  $V_{occ}$  is simply estimated by  $\left( \frac{4\pi R_g^3 N}{3} \right)$  where

$N$  is the number of chains (i.e. concentration) and  $R_g$  is calculated using the relationship provided in Ref 1. The scaling factor  $\alpha$  controls the gradient of this linear decrease and was found to give the best fit for  $\alpha = 0.74$ . We note that this value corresponds to the close-packing of spheres. Extensive results of PS 65k are shown in the main paper. Selected experimental results and self-consistent calculations for four different molecular weights ( $M_w$ ) are shown in Figure S1a and b. As expected from the model, increasing  $M_w$  and thus  $R_g$  should cause fullerene aggregation at a lower PS concentration. Calculations and experimental results are shown in Figure S1c, supporting this simple volume estimation for this system.

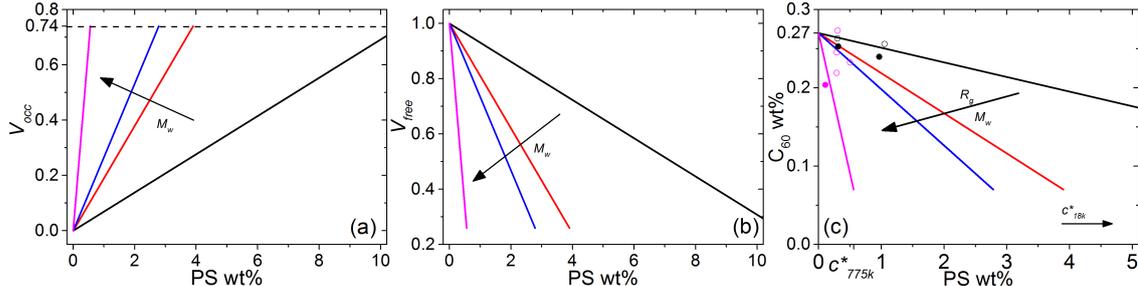


Figure S1: Scaling calculations for (a) occupied volume ( $V_{occ}$ ) and (b) free volume ( $V_{free}$ ) with four PS  $M_w$  shown. 18, 65, 100 and 775  $\text{kgmol}^{-1}$ . Dashed line indicates the volume at which maximum packing efficiency is achieved i.e.  $c^*$ . (c) Using the calculations described in the text, the modelled miscibility limit for  $C_{60}$  in PS/toluene is shown for 18, 65, 100 and 775  $\text{kgmol}^{-1}$ . Homogenous (●) and aggregated samples (○) are indicated in the relevant colour. Note that experiments were only carried out using 18 and 775  $\text{kgmol}^{-1}$  PS.

### S3 Film Thickness Control

In order to achieve similar film thicknesses from the same PS concentration via spon casting, it was necessary to find a PS concentration and rpm range in which this could be achieved. The initial thickness of annealed films can effect film morphology and so it was important to obtain the same film thickness in order to compare annealed morphologies. The result thickness/concentration/rpm map is shown in Figure S2 where an effective range to vary film thickness with polymer concentration is found from 500 to 7000 rpm. It was not possible to form a smooth film with 5 wt% 65k PS at 500 rpm.

### S4 Thin films and solution age

There is a time dependence to  $C_{60}$  cluster formation and size in solution. The clusters which are initially 100s nm evolve to form aggregates on the micron scale which eventually settle to the bottom of a stationary vessel. The morphology of thin films also depends on solution age, outside the miscibility window. In agreement to the results presented in the main paper for 130 nm and 5%  $C_{60}$ /PS, this effect is seen clearly with 60 nm thin films prepared with 9 wt %  $C_{60}$ . There is a clear dependence on the micron scale film morphology, shown in Fig S3. The as cast and annealed films prepared from the homogenous solution show no change in morphology with solution age, confirming the stability of the solution. In comparison very different morphologies with solution age are obtained when preparing films from solutions outside the miscibility window. The as cast film prepared from the precipitated, aged solution (Fig S3f) has large 10s  $\mu\text{m}$  sized features

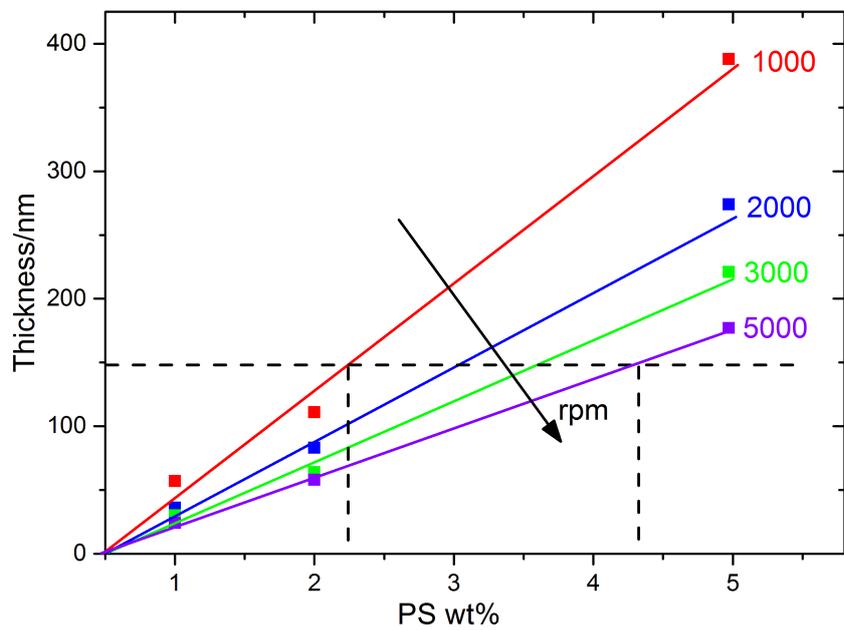


Figure S2: Calibration for varying PS concentration with spin coater RPM. Three PS concentrations are used: 1, 2 and 5 wt%. It is possible to achieve the same film thicknesses' from solutions starting at different concentrations.

present. Comparing the two annealed films (Fig S3d and h) again different morphologies are obtained.

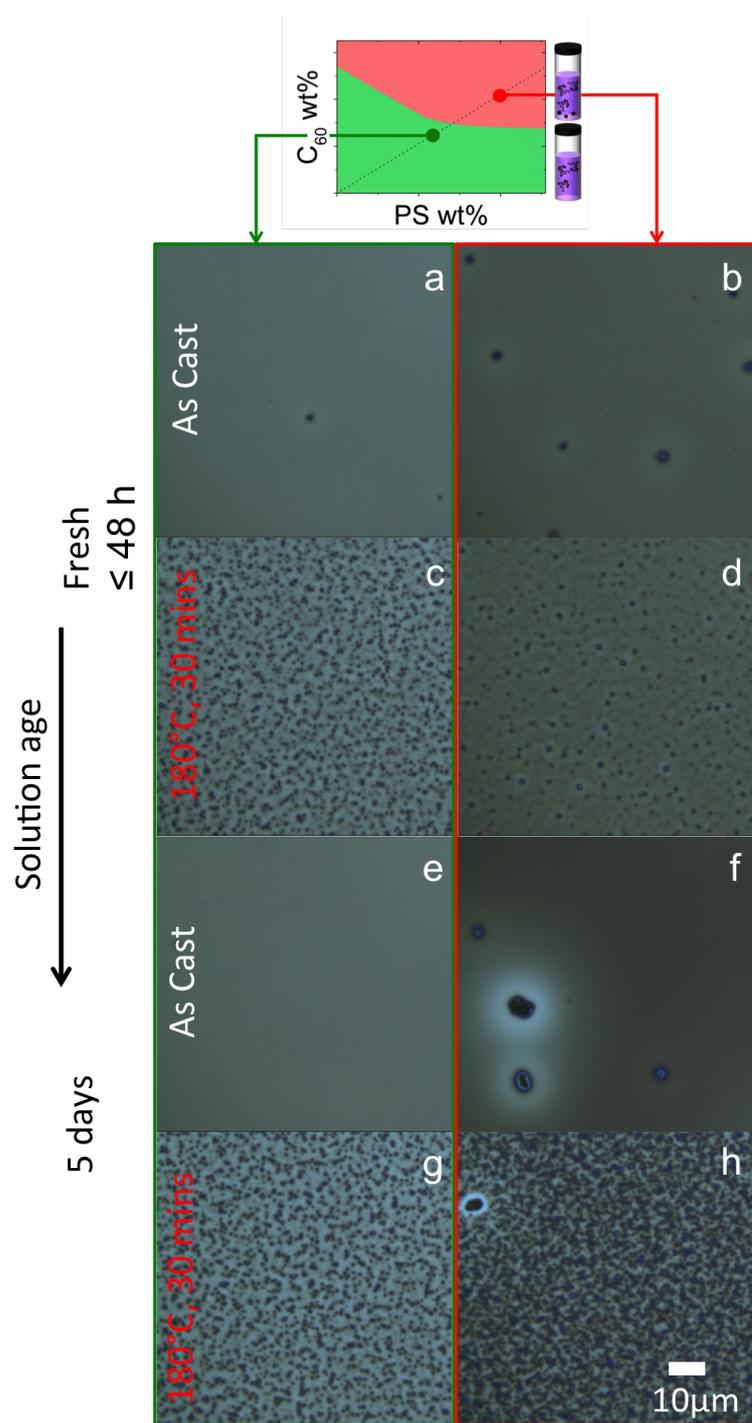


Figure S3: Optical microscopy images for 60 nm 9 wt% C<sub>60</sub>/PS thin films in the homogenous (a, c, e and g) and precipitated (b, d, f and h) regimes fabricated from fresh and aged solutions. As cast (a-b, e-f) films and those annealed at 180 °C for 30 minutes (c-d, g-h) films are shown.

## S5 Drop Cast

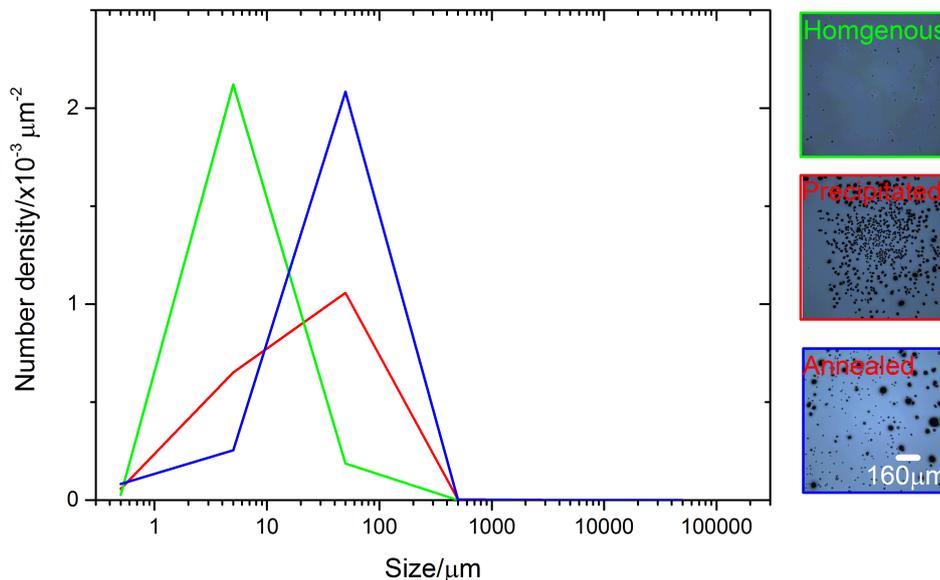


Figure S4: Number density of 4-7 representative images of the 5 wt%  $C_{60}$ /PS drop cast films. Image analysis was carried out on the as cast homogenous (green), as cast precipitated (red) and annealed precipitated (blue) samples. Reliable, consistent image analysis was not possible on the annealed homogenous film due to the open, stringy structure. Typical images are also show on the right hand side.

Comparing the number density of the as cast films it is clear that there are a significant number of larger clusters in films prepared from precipitated solutions (red line in Fig S4). Annealing this film leads to an increase in the number of these clusters. Clusters in films prepared from the homogenous solution are characteristically smaller which then go on to form open, stringy ('tumbleweed') structures.

## S6 Fullerenes with higher miscibility and less asymmetric solvents

To demonstrate the fullerene clustering phenomena with other fullerenes, two fullerene containing systems were studied: PCBM/PS/toluene (Fig. S5) and PCBM/PS/chlorobenzene (Fig. S6). In both cases a 775 kg/mol PS was used. There is a key difference between these two systems here and the  $C_{60}$ /PS/toluene mixtures, reported in the main paper: the miscibility limits of fullerenes in the different solvents, which are given in Table S2. The lower miscibilities of  $C_{60}$  and PCBM in toluene appears to induce fullerene aggregation upon the addition of PS. In contrast, PCBM is relatively more miscible in chlorobenzene and no PS-induced aggregation is observed in the same concentration range. In the context, of the simple volume argument presented above, by increasing the fullerene miscibility and reducing the solvent asymmetry, the parameter  $\alpha$  is reduced effectively to zero.

Table S2: Fullerene miscibility in solvents used in this study.

Fullerene	Solvent	Misc. limit (wt %)
C <sub>60</sub>	Toluene	0.27
PCBM	Toluene	0.9
PCBM	Chlorobenzene	2.7

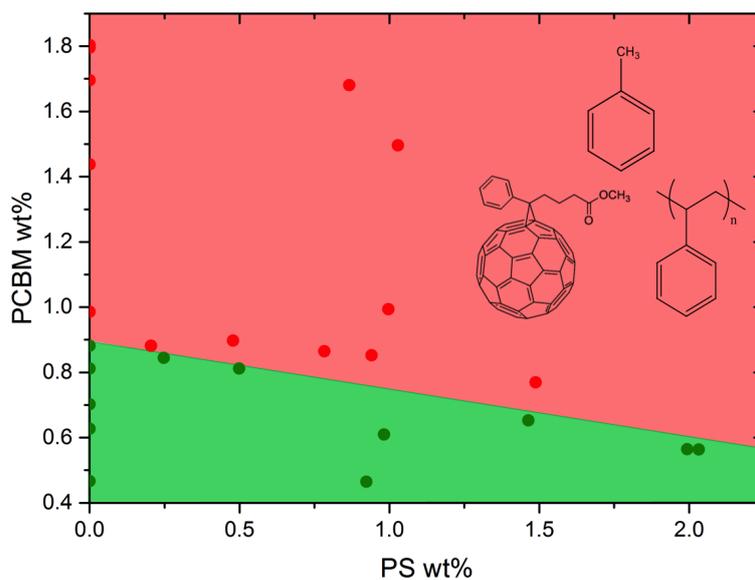


Figure S5: Diagram showing PCBM aggregation for a range of 775 kg/mol PS concentrations in toluene. Homogenous (●) and precipitated (●) solutions are shown. Polymer-induced fullerene aggregation is seen here.

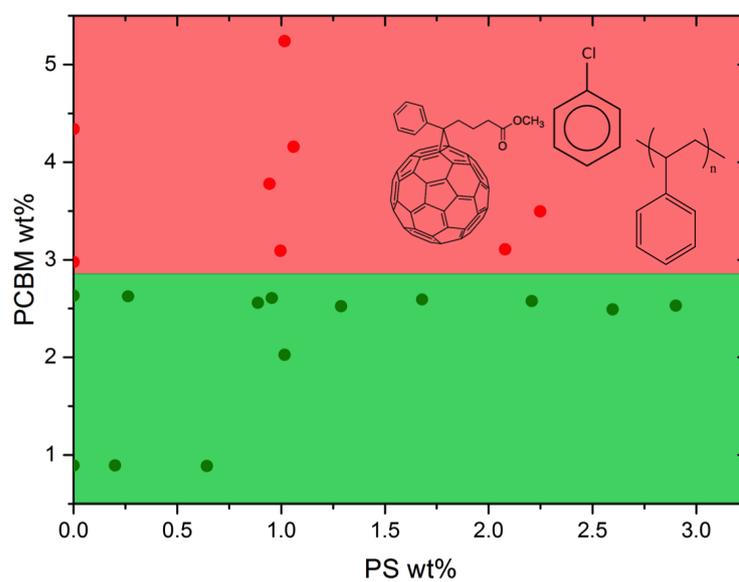


Figure S6: Diagram showing PCBM aggregation for a range of 775 kg/mol PS concentrations in chlorobenzene. Homogenous (●) and precipitated (●) solutions are shown. There is no indication of polymer-induced fullerene aggregation.

## References

- [1] K. Huber, S. Bantle, P. Lutz, and W. Burchard, “Hydrodynamic and thermodynamic behavior of short-chain polystyrene in toluene and cyclohexane at 34.5C,” *Macromolecules*, vol. 18, no. 7, pp. 1461–1467, 1985.