Experimental Report

15/10/2013

Proposal: **9-12-307** **Council:** 10/2011

Title: Dynamics of chain swelling in fullerene/polymer solutions: towards processing organic electronics

This proposal is a new proposal

Researh Area: Soft condensed matter

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Samples: hydrogenous polystyrene(C_8H_8)/fullerene (C_{60})/ deuterated toluene (C_7D_8)

Instrument	Req. Days	All. Days	From	To
D22	3	2	23/11/2012	25/11/2012

Abstract:

Organic electronics require solution-processed polymer/nanoparticle composites. The kinetics of polymer and nanoparticle behavior in solution effect the processing conditions needed. While the aggregation of C60 nanoparticles in toluene has been studied, only recently was it observed that there is a simultaneous swelling of the polystyrene chains. Solutions of polystyrene and C60 in toluene exhibit kinetic effects at two distinct length scales: chain swelling of the polymer (~1-4 nm) and aggregation of C60 NP’s (~ 1 micron). Understanding the relative rates of these two phenomena is necessary for determining the mechanism of chain swelling.

We propose to use SANS to quantify the kinetics of polystyrene chain swelling in toluene solutions with varying concentrations of C60. A control set of aged solutions will be used to determine the equilibrium state for each sample. Structure factors for polystyrene, measured using SANS, will be compared to optical, static- and dynamic- light scattering measurements for the kinetics of C60 aggregation. By quantifying the kinetics on both length scales, we hope to probe the interplay between chain swelling and C60 aggregation.

Dynamics of chain swelling in fullerene/polymer solutions: towards processing organic electronics

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Polymer:nanoparticle or small molecule composite thin films are viable for myriad applications, ranging from novel organic electronics to simple tribological modifiers. Solution-based processing remains the optimal fabrication method for such composites; however the behaviour of solutions is still not well-characterised. The thermodynamic forces that control the dispersion of polymer chains and nanoparticles in a common solvent control the ultimate morphology and physical properties of the resulting polymer composite when the solvent has been removed. [1] Here we have studied polymer conformation and fullerene aggregation in a ternary system containing polystyrene (PS), C_{60} and toluene across the dilute and semidilute regime, focussing on the structure and interaction strength of polymer/nanoparticle solutions with particular attention on the polymer length scales and the aggregation of the fullerenes.

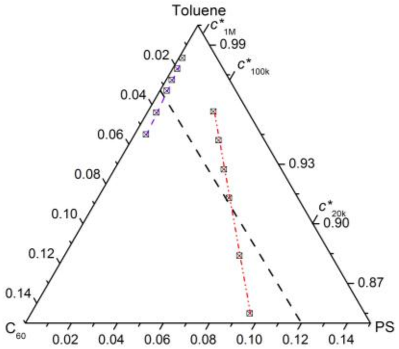

Figure 1: Ternary plot of two isopleths studied in this experiment PS:C_{60} (50:50 and 95:5), additionally it should be noted experiments were conducted above and below the C_{60} miscibility limit (c_{misc}) in toluene (black dashed line) [2]. The overlap concentrations (c*) for each M_w used are also shown.

As summarised in figure 1, two isopleths were studied, isopleth 1 was in a dilute solution using 100kgmol^{-1} PS where wt%C60/wt%PS=1. The second, isopleth 2 was in the semidilute regime, using 20, 100 and 1000 kgmol^{-1} PS, hereafter referred to as 20k, 100k and 1M, using wt%C60/wt%PS = 0.05. Additionally, two different SLD contrasts were used, Contrast A uses deuterated PS (PS-d) and C_{60} with hydrogenous toluene (Tol-h) (20k, 100k & 1M PS), so that the fullerene and polymer contributions can be observed. Contrast B uses hydrogenous PS (h-PS) and C_{60} in deuterated toluene (Tol-d) (100k), here only the polymer contribution to the scattering is observed. In the dilute regime, PS chains were fit using the PolymerExclVol model [3] in SasView. A detailed explanation can be found in reference [3]. For semidilute solutions, the Ornstein-Zernicke (OZ) form was used and the correlation length, ξ, fitted. This arises from introducing a Debye structure factor to the random phase approximation.[4] The scattering contribution from C_{60} was modeled using Aq^{-4}. This was regardless of whether the polymer was in the dilute or semidilute regimes, where $A = 2\pi\Delta\rho^2 S_V$, where S_V is the surface to volume ratio. Thus for isopleth 1 the R_g was found and quatified, as was ξ. Additionally S_v was quatified for the fullerene aggregates.

Figure 2 shows the coherent scattering intensities for all of the samples studied in both isopleths, along with the fits to the equations described above. Figure 2 (Left) shows PS in the dilute regime. The scaling exponent is expected to be 5/3 for a polymer in a good solvent (e.g. PS in toluene) and 2 for a Gaussian coil. Here, the exponent ranges from 1.66 to 1.85 for the samples investigated and is rather sensitive to background subtraction (which uses a ideal mixing assumption). This is in agreement with the expanded coil conformation expected for PS in a good solvent, additionally there is no change in R_g for the samples investigated within error when compared neat 100k PS in toluene (hollow symbols in the inset of Figure 2(Left)). The Flory-Huggins interaction parameter , was also found for the solutions in isopleth 1 to be in the region of 0.44 to 0.48, these values are within those previously found in literature.[5] Thus, we have clearly demonstrated with the use of

SANS, that there is no change in PS R_g and upon the addition of up to 0.4wt% C_{60} in the dilute regime when compared to neat PS. It should be noted that we have also shown this with the use of SLS and DLS.

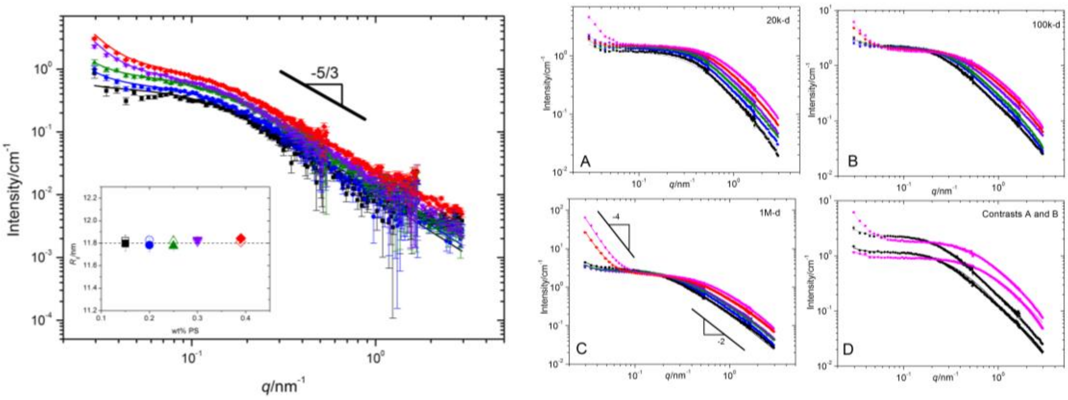

Figure 2: (Left) Coherent scattering intensity from small angle neutron scattering for 100k PS for Isopleth 1 (wt%C60/wt%PS=1). wt% C_{60} = 0.15, 0.2, 0.25, 0.3, 0.4 and 0.5. The inset shows fitted R_g for PS with C_{60} (filled symbols) and without (hollow symbols), the dashed line is a guide to the eye and is calculated using R_g=0.0125$M_w^{0.595}$ [6]. (Right) Coherent scattering intensity from small angle neutron scattering for isopleth 2 (wt%C_{60}/wt%PS = 0.05%). A-C use contrast A (PS-d, C_{60} and tol-h); wt% C60 = 0.15, 0.2, 0.25, 0.3, 0.4 and 0.5. D is a comparison for contrast A (Circles) and B (Squares) (PS-h, C_{60} and Tol-d) to demonstrate the low q upturn was due to scattering contributions from C_{60}.

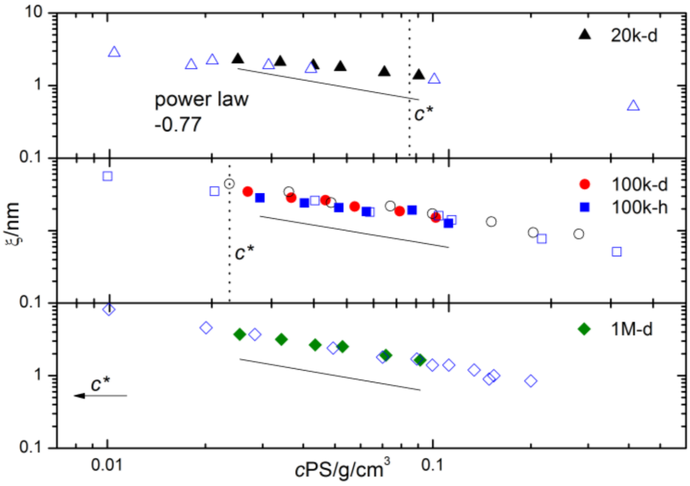

Figure 3: Fitted ξ against concentration of the PS in the overall solution from the SANS data shown in Figure 9 (filled symbols).The hollow symbols are for similar molecular weights from King *et al* (100kDa)[7] (black) and Hamada *et al* (17.5k, 110k & 900kDa)[8] (blue). Dashed lines indicate c* for the 20k and 100k. c* for 1M is not on this scale, as indicated.

Figure 3 summarieses the PS correlation length with comparison to previous literature on PS/toluene solutions. There is clearly no change in the correlation legnth either above or below c* and with respect of c_{misc}. The fitted ξ for isopleth 2 also falls onto a master curve with the correlation length reduced by a constant R_g, calculated using R_g =0.0125$M_w^{0.595}$ [7], and concentration reduced by c*. As expected the data fall onto a single line, described by $(1 + \beta c/c^*)^{\alpha}$, where β =4 and α=-0.77, the expected exponenet for semidilute polymer solutions in a good solvent.[9]

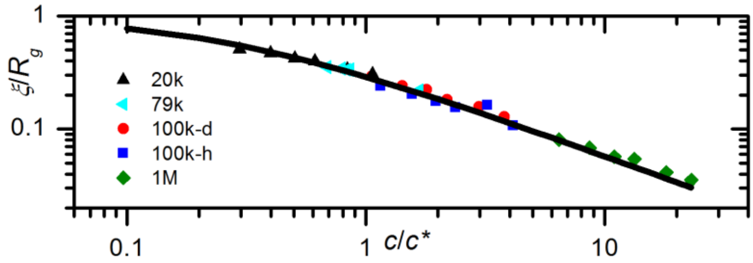

Figure 4: Reduced correlation length ξ/R_g of data from both isopleths plotted against reduced concentration c/c^*. A line of best fit of the form $(1 + \beta c/c^*)^{\alpha}$, where $\beta = 4$ and $\alpha = -0.77$.[9] The R_g used was calculated using $R_g = 0.0125 M_w^{0.595}$ [7].

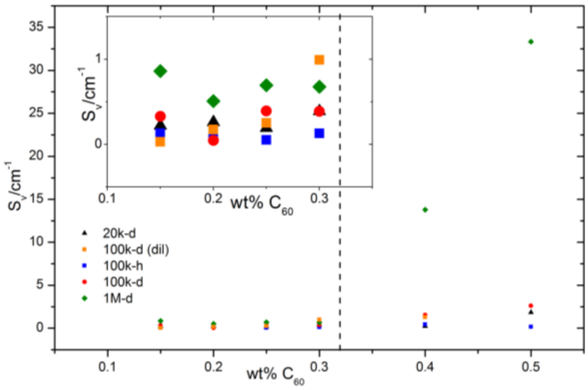

Figure 5: S_V for the three molecular weights (20k, 100k and 1M) studied on isopleth 1 and 2. The dashed black line is the previously determined c_{misc} of C_{60} in toluene (0.32wt%) by Rou et al [33]. The values for S_V from the dilute 100k-d PS (100k-d dil) seen in isopleth 1 is also included. The data for 100k-h is included as a baseline for which the C_{60} aggregation is not observed due to contrast matching. The inset focuses on the region below c_{misc}.

In summary, we have shown the R_g for PS in dilute solutions (isopleth 1) is unchanged upon addition of C_{60}, there is no change in the solvent quality experienced by the individual PS chains in the concentration range measured for PS (0.15 to 0.4wt%) and C_{60} (0.15 to 0.4wt%). The R_g measured is the expected value using the relationship provided by Huber *et al*, $R_g = 0.0125 M_w^{0.595}$ [7].

In the semidilute regime, the ξ fit to PS toluene solutions containing C_{60} (isopleth 2) are equivalent to the data obtained by King *et al* [7] and Hamada *et al* [8]. This demonstrates that this is no change in ξ of PS in toluene when C_{60} is added to the system. There is a clear increase in the scattering intensity at low q from SANS when the C_{60} wt% is higher than c_{misc}. The S_V calculated from this scattering contribution is M_w dependant, where the higher M_w (1M) results in a higher S_V. Thus, we conclude the increasing the M_w of PS results in the C_{60} aggregates experiencing an osmotic pressure sooner than with a lower M_w (20k), i.e. the size of the depletion layer is larger with a higher M_w and there is less space for the C_{60} aggregates to be. Additionally, there is also no change in ξ comparing neat PS to 0.96wt% C_{60} loaded PS toluene solutions, the reduced correlation length and concentration can fall on to a master curve with a power law of -0.77, expected for PS in a good solvent. Future work could potentially consist of studies with alternate fullerenes, nanoparticles and polymers in addition to a variety of solvents and solvent mixtures.

References

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