

Clustering of high molecular weight PCDTBT in bulk-heterojunction casting solutions

Andrew J. Clulow,*¹ Elliot P. Gilbert,² Pascal Wolfer,¹ Paul L. Burn*¹ and Ian R. Gentle¹

¹ *Centre for Organic Photonics & Electronics, The University of Queensland, St Lucia, QLD 4072, Australia.*

² *Bragg Institute, Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia.*

Email: a.clulow@uq.edu.au, p.burn2@uq.edu.au

Phone: +61 7 3365 3778

Fax: +61 7 3346 9273

Abstract

The narrow optical gap conjugated polymer poly[*N*-9''-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) has been used as the electron donor material in efficient solution-processed bulk-heterojunction (BHJ) photovoltaic and photodetector devices when blended with fullerene derivatives. It was found that the solution viscosity used to form the active films could be controlled by the cooling rate of a hot solution of the materials and that fast-cooled solutions afforded more efficient bulk-heterojunction solar cells than their slow-cooled counterparts. Viscometry measurements showed that the rheological behaviour of the solutions is modelled by the Martin equation for different PCDTBT molecular weights and temperatures. The Martin constant K_M that describes the inter-polymer interactions in solution was found to increase with polymer molecular weight and decrease with increasing temperature in an analogous manner to the Flory-Huggins interaction parameter χ . Small Angle Neutron Scattering (SANS) was used to show that when hot solutions of the polymer were cooled, phase separation into polymer-rich clusters and solvent rich domains occurred. In the case of the blend solutions similar phase separation was observed. In addition, the fast-cooled solutions trapped more 70-PCBM in the polymer rich phase, which in turn made the structure of the polymer more rod-like in clusters. The results provide an explanation as to why fast-cooled solutions lead to devices with greater efficiency.

Introduction

The active layers of organic solar cells (OSCs) and photodiodes based on polymer/fullerene blends are typically deposited from solution onto a suitable substrate to form a thin film. It is now well established that the morphology of the films thus formed plays a crucial role in device performance. The most efficient devices typically have a bulk-heterojunction (BHJ) morphology, which are considered to have phase separated domains of polymer and fullerene intermixed with blended regions.¹⁻³ For many years much emphasis has been placed on post-deposition treatments to optimise the active layer morphologies and improve device performance, with thermal and solvent annealing being the most popular methods. However, more recently the structuring of molecules in solution prior to and during solution-based deposition has emerged as a factor in determining device efficiency.⁴⁻⁵

Poly(*n*-alkylthiophenes) have received attention in this regard, with gelation in solution being induced by decreasing solution temperatures, co-dissolution in marginal solvents or a combination of the two.⁶⁻⁹ Such polymers are typically semi-crystalline forming lamellae in thin films through interactions between the pendant linear alkyl chains along their backbones. Such crystallisation provides a clear mechanism for gelation in solution as the solvent quality decreases and has been used as the basis for modelling their structures in solution. However, the low-optical gap polymer poly[*N*-9''-hepta-decanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT, Scheme 1), which is typically amorphous in thin films, also shows solution structuring effects and when blended with the fullerene 70-PCBM gives better power conversion efficiencies than the poly(*n*-alkylthiophenes) (Scheme 1).¹⁰⁻¹¹ Marginal solvents used in preparation of thin films can also be used to impart crystallinity to PCDTBT.¹² However, it has been shown that even in a nominally good solvent for PCDTBT that is typically employed in its deposition (1,2-dichlorobenzene, DCB) the polymer molecular weight and the method of solution preparation strongly influence the solution rheology and the resulting device performance.⁴ Hot solutions containing high \bar{M}_w PCDTBT form a gel if cooled too rapidly but remain fluid if cooled

Chromatography (GPC) in 1,2,4-trichlorobenzene at 135 °C by SJPC, Canada. 70-PCBM was purchased from American Dye Source, Inc. and used as received. 1,2-Dichlorobenzene (anhydrous) and 1,2-dichlorobenzene- d_4 (D, 99%) were purchased from Sigma Aldrich and Cambridge Isotope Laboratories, respectively, and were used as received. Solutions for the SANS measurements were prepared as previously reported⁴ using a Stuart Heat Stir CB162 hotplate monitored with a thermocouple. All of the solutions measured had a PCDTBT concentration of 5 mg mL⁻¹ and blend solutions had a 70-PCBM concentration of 20 mg mL⁻¹, corresponding to the 1:4 ratio by weight of the materials that leads to efficient devices.^{10, 14-16}

Viscometry Measurements. The experimental conditions used for the viscometry measurements were reported previously.⁴ Solutions for kinematic viscosity measurements were prepared by dissolving the PCDTBT or the PCDTBT/70-PCBM blend components in 1,2-dichlorobenzene at 140 °C. After complete dissolution, the hot-plate was switched off and the solutions were allowed to cool to room temperature with a resulting average cooling rate of around 1.5 °C min⁻¹. Subsequently, 0.7 mL of solution were transferred into an Ostwald Micro Viscometer for analysis. Kinematic viscosities were determined using an Ostwald Micro Viscometer with a viscometer constant of 0.075 at 20 °C. For viscosity measurements performed at elevated temperatures, the viscometer constant was calibrated with 1,2-ethanediol. For measurements conducted at 20 °C, the viscometer was immersed in a temperature-controlled water bath. For experiments performed in the temperature range between 40 and 140 °C, the viscometer was placed in a temperature-controlled and thermally insulated oil bath. Solutions were allowed to equilibrate at the desired temperature for 15 min prior to analysis and viscosity values were averaged over 5 measurements.

Small Angle Neutron Scattering (SANS) Experiments. SANS measurements were performed on the Quokka instrument at OPAL¹⁷ with neutrons of wavelength of 5.0 Å ($\Delta\lambda/\lambda = 10\%$). Two instrument configurations were used with equal source-to-sample and sample to detector distances of 20 and 4 m, the latter with a 300 mm lateral detector offset to increase the maximum Q , with

source and sample aperture diameters of 50 mm and 10 mm respectively. These configurations provide a continuous Q range of 0.004 to 0.284 \AA^{-1} where Q is the magnitude of the scattering vector, defined by $Q = (4\pi/\lambda)\sin(\theta)$, λ is the neutron wavelength, and 2θ is the scattering angle. All samples were enclosed in demountable cells with a 1 mm path length. Sample temperature was controlled by a Julabo thermostatted bath. Slow- and fast-cooled PCDTBT, 70-PCBM and PCDTBT/70-PCBM blend (1:4 w/w) solutions were prepared using the procedures reported previously for the fabrication of OPV devices.⁴ To prepare the blend solutions, solutions of PCDTBT (7.5 mg mL^{-1}) and 70-PCBM (60 mg mL^{-1}) were prepared in 1,2-dichlorobenzene- d_4 and 1,2-dichlorobenzene by dissolving the solids at $140 \text{ }^\circ\text{C}$. The temperature of the hotplate was gradually lowered to $90 \text{ }^\circ\text{C}$ and the PCDTBT and 70-PCBM solutions were combined in a 2:1 v/v ratio to obtain a PCDTBT/70-PCBM ratio in solution of 1:4 w/w and a total concentration of 25 mg mL^{-1} . After stirring at $90 \text{ }^\circ\text{C}$ for around 10 min, the solution was split into two equal fractions. The first fraction was immediately removed from the hot-plate and placed on a metal surface at room temperature for the fast-cooled sample. Subsequently, the hot-plate was switched off and allowed to slowly cool to room temperature with the second fraction still on the plate, resulting in an average cooling rate of about $1.5 \text{ }^\circ\text{C min}^{-1}$ for the slow-cooled sample. The same thermal treatments were used to prepare slow- and fast-cooled PCDTBT (5 mg mL^{-1}) solutions in 1,2-dichlorobenzene- d_4 and 70-PCBM (20 mg mL^{-1}) in 1,2-dichlorobenzene for comparison. Solutions were measured in their slow-cooled or fast-cooled state at $25 \text{ }^\circ\text{C}$ before they were re-heated to $90 \text{ }^\circ\text{C}$ with the initially slow-cooled solutions being re-measured in their hot state. All data were corrected for blocked beam measurements, normalized, radially averaged and placed on an absolute scale, following attenuated direct beam measurements, using a package of macros in Igor Pro software (Wavemetrics, Lake Oswego, OR, U.S.A.), and modified to accept HDF5 data files from Quokka.¹⁸ The SANS profiles were fitted using the ‘Polymer-Excluded Volume’ and ‘Correlation Length’ models from the NCNR analysis macros built in to the analysis software.

Results and Discussion

The viscometry data for the PCDTBT and PCDTBT/70-PCBM solutions are given in Figure 1.⁴ The data could not be fitted using the traditional Huggins-Kraemer analysis applied to dilute polymer solutions and so the data was fitted with the Martin equation (1) that can be used to describe the viscosity of dilute and moderately concentrated polymer solutions¹⁹⁻²¹

$$\ln\left(\frac{\eta - \eta_0}{c\eta_0}\right) = \ln\left(\frac{\eta_{sp}}{c}\right) = \ln[\eta] + K_M c[\eta], \quad (1)$$

where η is the solution viscosity, η_0 is the solvent viscosity at the same temperature, c is the solution concentration, η_{sp} is the specific viscosity, $[\eta]$ is the intrinsic viscosity of the polymer and K_M is the Martin constant, which is a measure of polymer-polymer interactions. The fitting parameters are summarised in Table 1.

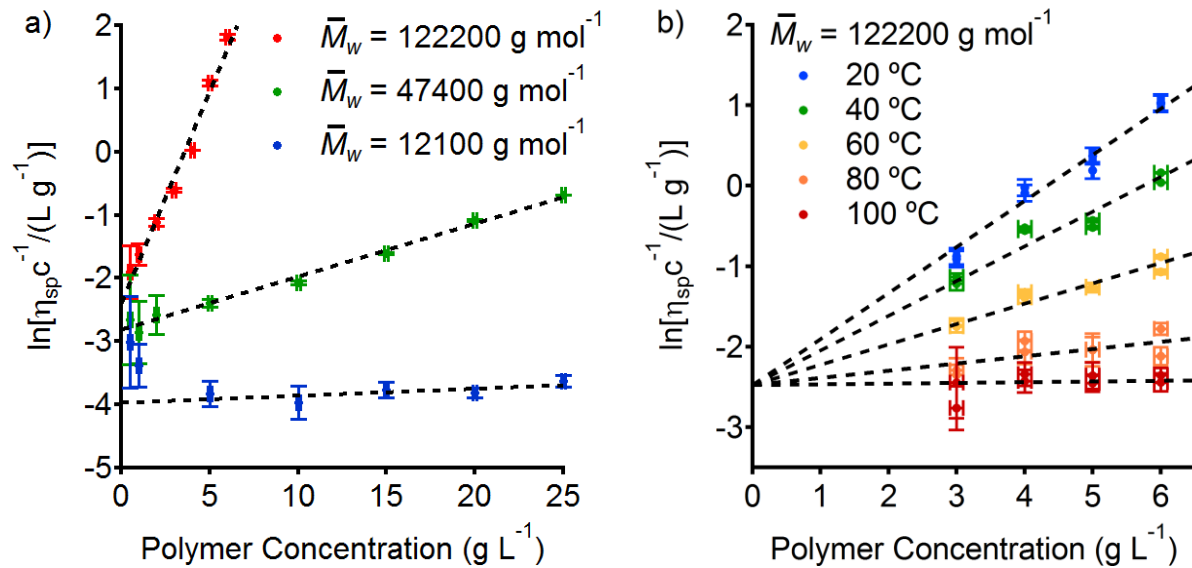


Figure 1 a) Variations in viscosity of different molecular weight PCDTBT solutions in 1,2-dichlorobenzene as a function of concentration at 20 °C. b) Viscosity variations for both PCDTBT ($\bar{M}_w = 122200 \text{ g mol}^{-1}$) and 1:4 blend solutions in 1,2-dichlorobenzene as a function of concentration at different temperatures.

PCDTBT \bar{M}_w (g mol^{-1})	$\ln\{[\eta]/(\text{L g}^{-1})\}$	K_M	$[\eta]$ (L g^{-1})	R_{Hyd} (\AA)	c^* (g L^{-1})
12100	-3.97 ± 0.10	0.58 ± 0.22	$(1.89 \pm 0.19) \times 10^{-2}$	33 ± 2	132 ± 13
47400	-2.81 ± 0.05	1.41 ± 0.12	$(6.02 \pm 0.30) \times 10^{-2}$	77 ± 2	42 ± 2
122200	-2.39 ± 0.15	7.33 ± 0.45	$(9.16 \pm 1.37) \times 10^{-2}$	121 ± 10	27 ± 4

122200 (variable temperature)	-2.48 ± 0.09	Temperature dependent	$(8.37 \pm 0.75) \times 10^{-2}$	117 ± 6	30 ± 3
-------------------------------	------------------	-----------------------	----------------------------------	-------------	------------

Table 1 Intrinsic viscosities and Martin constants from fitting of the data in Figure 1 to the Martin equation along with corresponding hydrodynamic radii (R_{Hyd}) for equivalent spheres [from Equation (2)] and overlap concentrations c^* [from Equation (3)]. The uncertainties in $\ln[\eta]$ and K_M were determined from the least squares fitting to the data in Figure 1 and propagated using the chain rule to determine the uncertainties in $[\eta]$, R_{Hyd} and c^* .

The data in Figure 1 a) for PCDTBT of different molecular weights shows that the intrinsic viscosity $[\eta]$ increases with polymer molecular weight as expected. The Martin constant K_M also increases with polymer molecular weight indicating stronger interchain interactions with increasing degree of polymerization. The temperature-dependent viscometry data [Figure 1 b)] for both the PCDTBT and blend solutions with a common molecular weight ($\bar{M}_w = 122200 \text{ g mol}^{-1}$) can be fitted with a common intrinsic viscosity, which is within experimental error of the value obtained for the analogous fit in Figure 1 a). The corresponding Mark-Houwink-Sakurada plot of $\ln([\eta])$ against $\ln(\bar{M}_w)$ is given in Figure 2 a) and shows the expected linear dependence. The gradient of the Mark-Houwink plot is 0.68 ± 0.03 , which is consistent with polymer coils dissolved in a good solvent.²²

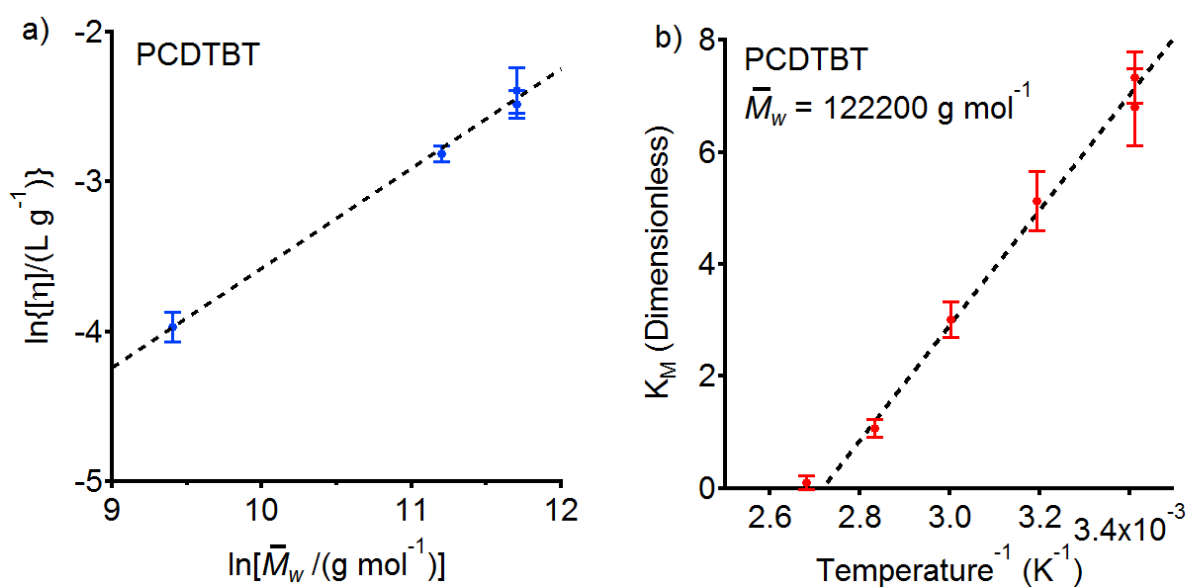


Figure 2 a) Mark-Houwink-Sakurada plot for PCDTBT in 1,2-dichlorobenzene solution. The two data points at $\bar{M}_w = 122200 \text{ g mol}^{-1}$ are the intrinsic viscosities from Figures 1 a) and 1 b). **b)**

Variation of the Martin constant K_M with inverse absolute temperature. The two data points at $T = 293$ K correspond to the Martin constants from Figures 1 a) and 1 b).

The intrinsic viscosities determined from the viscometry data were used to estimate the hydrodynamic volumes and radii for each batch of PCDTBT using a rearrangement of the Einstein viscosity equation for hydrodynamically non-interacting spheres at infinite dilution²²

$$\left(\frac{\eta_{sp}}{c}\right)_{c \rightarrow 0} = [\eta] = 2.5 \left(\frac{N_{Av} V_{Hyd}}{\bar{M}_w}\right), \quad (2)$$

where N_{Av} is Avogadro's number and V_{Hyd} is the hydrodynamic volume. The overlap concentration (c^* , at which the average local concentration within each polymer coil is equal to the solution concentration) can then be estimated from Equation (2) and the intrinsic viscosities from

$$c^* \approx \frac{\bar{M}_w}{N_{Av} V_{Hyd}} = \frac{2.5}{[\eta]}. \quad (3)$$

The hydrodynamic volume, radii and overlap concentrations determined using Equations (2) and (3) are summarised in Table 1. The calculated overlap concentrations c^* are all greater than the maximum solution concentrations tested for each batch of PCDTBT, indicating that under the conditions examined the polymer coils are on average below the overlap threshold for individual, well dispersed spheres. The exponential increase in viscosity with polymer concentration cannot therefore be interpreted as forced entanglement of the polymer chains due to close packing but must be related to the interactions between polymer chains within the solvent characterised by the Martin constant K_M . Figure 1 shows that K_M increases with increasing polymer molecular weight and as the temperature of either PCDTBT or blend solution was decreased. The data in Figure 2 b) shows that K_M increased linearly with inverse temperature within the temperature range examined leading to an Arrhenius-type form of the Martin equation given by

$$\frac{\eta - \eta_0}{\eta_0} = [\eta] c \exp \left\{ \left[\frac{(10300 \pm 500)}{T} - (27.9 \pm 1.7) \right] [\eta] c \right\}, \quad (4)$$

where $[\eta] = (8.37 \pm 0.75) \times 10^{-2} \text{ L g}^{-1}$. This implies that there is an apparent activation energy of $85.6 \pm 4.2 \text{ kJ mol}^{-1}$ to overcome the interactions between PCDTBT chains with an

$\bar{M}_w = 122200 \text{ g mol}^{-1}$. The interactions were predicted to be quenched at 96 °C and the observed Martin constant at 100 °C is within error of zero with the solutions having viscosities similar to that of the neat solvent.

To complete the study SANS experiments were performed to examine polymer conformation and large-scale structure formation in solution under thermal cycling. SANS profiles for $\bar{M}_w = 122200 \text{ g mol}^{-1}$ PCDTBT and 1:4 blends with 70-PCBM in 1,2-dichlorobenzene- d_4 (d_4 -DCB) are depicted in Figure 3. Due to the poor contrast in neutron scattering length density (SLD) between 70-PCBM (SLD = $4.74 \times 10^{-6} \text{ \AA}^{-2}$)²³ and d_4 -DCB (SLD = $4.58 \times 10^{-6} \text{ \AA}^{-2}$)²⁴ only structuring of the PCDTBT (SLD = $1.42 \times 10^{-6} \text{ \AA}^{-2}$)²³ may be observed in these SANS profiles. Negligible scattering intensity was observed for 70-PCBM and PCDTBT/70-PCBM blend solutions in h_4 -DCB (SLD = $2.35 \times 10^{-6} \text{ \AA}^{-2}$)²⁴ (Figure S1), consistent with prior reports of SANS measurements on fullerenes in 1,2-dichlorobenzene.⁶ It was immediately apparent from the SANS measurements in d_4 -DCB that the addition of the fullerene had only subtle effects on the polymer structures. The SANS spectra for the solutions at 90 °C (Figure 3) were consistent with expanded polymer coils in solution as indicated by the Mark-Houwink-Sakurada analysis. These profiles were fitted as polymers with an excluded volume parameter for a self-avoiding walk (Porod exponent = 5/3). The calculated radii of gyration of 112 ± 3 and $107 \pm 2 \text{ \AA}$ (Table 2) determined for the polymer and blend solutions respectively are within error of the hydrodynamic radii of around 110-130 \AA determined from the intrinsic viscosities of the $\bar{M}_w = 122200 \text{ g mol}^{-1}$ PCDTBT (Table 1). Therefore at high temperatures the PCDTBT chains appear to be well dissolved in dichlorobenzene.

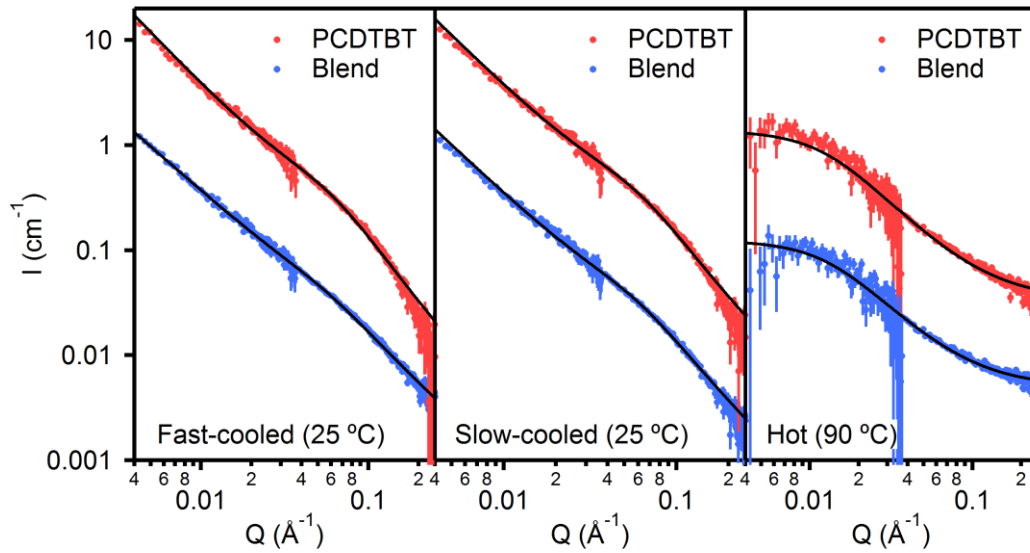


Figure 3 Measured SANS profiles (absolute scaling) of hot, slow-cooled and fast-cooled PCDTBT and 1:4 blend solutions in d_4 -DCB. $c_{PCDTBT} = 5 \text{ mg mL}^{-1}$ in all solutions and $c_{70-PCBM} = 20 \text{ mg mL}^{-1}$ in the blend solutions. Points indicate reduced data and solid lines are the fits to the data. In each plot the PCDTBT solution data is offset above the 1:4 blend data by a factor of 10 for clarity.

Sample	$I(Q=0) \text{ (cm}^{-1}\text{)}$	$R_g \text{ (}\text{\AA}\text{)}$	Porod Exponent
Hot PCDTBT	0.136 ± 0.005	112 ± 3	1.67 (fixed)
Hot Blend	0.120 ± 0.004	107 ± 2	1.67 (fixed)

Table 2 Polymer excluded volume fitting parameters for the hot PCDTBT and Blend samples.

When the solutions were cooled (either quickly or slowly) to 25 °C, the SANS intensity at low- Q increased sharply indicating the formation of larger structures in the solution. A second structural feature at high- Q is also apparent in the spectra. The data were fitted using the correlation length model developed by Hammouda *et al.*²⁵⁻²⁸ to describe clustering in polymer solutions

$$I(Q) = \frac{A}{Q^n} + \frac{C}{[1 + (Q\xi)^m]} + B. \quad (5)$$

The power law (A -term) represents Porod's law scattering from large clusters at low- Q , while the Lorentzian (C -term) describes the local polymer-solvent interactions within the correlation length ξ at high- Q . The fit parameters for the models are given in Table 3.

Sample	Porod Scale, A ($\times 10^{-4} \text{ cm}^{-1}$)	Porod Exponent, n	Lorentzian Scale, C	Lorentzian Exponent, m	Correlation Length, $\xi \text{ (}\text{\AA}\text{)}$

			($\times 10^{-2} \text{ cm}^{-1}$)		
Slow-cooled PCDTBT	1.9 ± 0.1	1.63 ± 0.01	3.0 ± 0.1	3 (fixed)	16 (fixed)
Fast-cooled PCDTBT	1.6 ± 0.1	1.68 ± 0.01	2.9 ± 0.1	3 (fixed)	16 (fixed)
Slow-cooled Blend	2.4 ± 0.1	1.57 ± 0.01	2.3 ± 0.1	3 (fixed)	16 (fixed)
Fast-cooled Blend	5.1 ± 0.1	1.42 ± 0.01	1.6 ± 0.1	3 (fixed)	16 (fixed)

Table 3 Correlation length model fitting parameters for the cooled PCDTBT and blend samples.

The Porod exponents n of 1.4-1.7 indicate fractal dimensions consistent with semi-flexible and expanded polymer chains inside the clusters, as was seen in the case of the hot solutions. In each model the Lorentzian exponents m and the correlation lengths ζ had similar optimum values of around 3 and 16 Å, respectively, which were then used as fixed parameters in the modelling. The Lorentzian exponent of 3 corresponds to a self-attractive walk, thus within the correlation lengths of 16 Å, the PCDTBT chains collapse or aggregate with each other. This suggests that phase separation into large polymer-rich clusters comprising expanded polymer coils and solvent-rich regions containing isolated collapsed polymer chains is occurring. Such a transition is predicted to occur as the Flory-Huggins interaction parameter χ increases and attractive interactions between the monomer units in the solution become stronger.²⁹ This correlates well with the viscometry data as the Martin constant K_M describing the polymer-polymer interactions in solution increases linearly with inverse temperature, which is how χ is expected to vary.

The relative magnitudes of the Porod and Lorentzian components and the Porod exponents were similar for both slow- and fast-cooled PCDTBT solutions consistent with the limited differences in their SANS profiles. No low- Q plateau was observed in the data meaning that the sizes of the polymer clusters were indeterminable from these SANS measurements but are far greater than Q_{min}^{-1} . In the case of the blend solutions however, fast-cooling leads to an increase in the magnitude of the Porod component at the expense of the Lorentzian component when compared with the slow-cooled solution. This suggests that there is greater clustering in the fast-cooled

solution, which might be expected to lead to the greater solution viscosities observed for the fast-cooled blends.⁴ The Porod exponents of the blend solutions also deviate more strongly from the ideal value of 1.67 for self-avoiding walks towards that of the semi-flexible regime. The fast-cooled solution has a lower Porod exponent, suggesting that the chains are more rod-like in these clusters than in the slow-cooled solutions. We posit that this is due to the trapping of 70-PCBM molecules inside the clusters upon their formation. In the fast-cooled solutions the polymer rich phase will form more rapidly as the critical point is reached, trapping the fullerenes in the polymer rich phase. In contrast, in the slow-cooled solutions the fullerene molecules have more time to emerge from the polymer clusters and be dissolved in the solvent rich phase. Thus the cooling rate of the PCDTBT:70-PCBM solutions determines how finely intermixed the polymer and fullerene will be in a the thin film cast from the solution. As such, the better performance of operational organic solar cells prepared from fast-cooled blend solutions can be explained by higher PCDTBT:70-PCBM blend ratios in the clusters formed prior to film deposition that lead to a more finely intermixed bulk heterojunction active layer.⁴

Conclusions

The combined viscometry and SANS measurements provide a clear explanation for the effect of PCDTBT:70-PCBM solution preparation on viscosity and device performance. The viscometry data could be described by the Martin equation with an interaction constant K_M that increased with PCDTBT molecular weight. The variation in intrinsic viscosity with PCDTBT molecular weight suggested that the polymer chains were well dissolved in 1,2-dichlorobenzene at vanishingly low concentrations. This was also observed by SANS measurements on hot PCDTBT and blend solutions, which showed the polymer chains to take self-avoiding walks with radii of gyration similar to the hydrodynamic radii calculated from the intrinsic viscosity of the polymer. Upon cooling the solutions, SANS revealed phase separation into large polymer-rich clusters and solvent-rich regions with isolated collapsed polymer chains. This phase separation process was linked to the declining quality of the solvent as the temperature was reduced, with the Martin

constant K_M increasing with inverse temperature in a manner analogous to that expected of the Flory-Huggins interaction parameter χ . The rate of cluster formation in the blend solutions appears to be critical to the structuring inside the clusters, with fast-cooled solutions yielding more rod-like chains arranged around trapped fullerenes. That is, the fast-cooled solutions lead to a more finely mixed bulk heterojunction prior to deposition than the slow-cooled counterparts and with a corresponding enhancement in device performance.

Acknowledgements

The authors would like to thank Dr Norman Booth for his assistance with the sample environments for this experiment. The authors would also like to thank Dr Andrew Nelson for his assistance with experiment proposal preparation. This work has been supported by the Australian Research Council (DP120101372). PW would like to thank the Swiss National Science Foundation (SNSF) for an Advanced Researcher Fellowship (PA00P2_145395). PLB is supported by University of Queensland Vice Chancellor's Research Focussed Fellowship. We acknowledge funding from the University of Queensland (Strategic Initiative – Centre for Organic Photonics & Electronics) and the Queensland Government (National and International Research Alliances Program). We acknowledge the support of the Bragg Institute, the Australian Nuclear Science and Technology Organisation (ANSTO) and the Australian Institute for Nuclear Science and Engineering (AINSE) in providing the neutron research facilities used in this work.

Supporting Information

A supporting information file is available containing the SANS intensity *versus* Q plots for 70-PCBM and PCDTBT/70-PCBM (1:4 w/w) blend solutions in h_4 -DCB.

References

- (1) Yin, W.; Dadmun, M., *ACS Nano* **2011**, *5*, 4756-4768.
- (2) Buchaca-Domingo, E.; Ferguson, A. J.; Jamieson, F. C.; McCarthy-Ward, T.; Shoaee, S.; Tumbleston, J. R.; Reid, O. G.; Yu, L.; Madec, M. B.; Pfannmoller, M.; Hermerschmidt, F.; Schroder, R. R.; Watkins, S. E.; Kopidakis, N.; Portale, G.; Amassian, A.; Heeney, M.; Ade, H.; Rumbles, G.; Durrant, J. R.; Stingelin, N., *Mater. Horiz.* **2014**, *1*, 270-279.
- (3) Treat, N. D.; Chabinyk, M. L., *Annu. Rev. Phys. Chem.* **2014**, *65*, 59-81.
- (4) Wolfer, P.; Armin, A.; Pivrikas, A.; Velusamy, M.; Burn, P. L.; Meredith, P., *J. Mater. Chem. C* **2014**, *2*, 71-77.
- (5) Liu, Y.; Zhao, J.; Li, Z.; Mu, C.; Ma, W.; Hu, H.; Jiang, K.; Lin, H.; Ade, H.; Yan, H., *Nat. Commun.* **2014**, *5*, 5293.
- (6) Sobkowicz, M. J.; Jones, R. L.; Kline, R. J.; DeLongchamp, D. M., *Macromolecules* **2011**, *45*, 1046-1055.
- (7) Newbloom, G. M.; Weigandt, K. M.; Pozzo, D. C., *Soft Matter* **2012**, *8*, 8854-8864.
- (8) Keum, J. K.; Xiao, K.; Ivanov, I. N.; Hong, K.; Browning, J. F.; Smith, G. S.; Shao, M.; Littrell, K. C.; Rondinone, A. J.; Andrew Payzant, E.; Chen, J.; Hensley, D. K., *CrystEngComm* **2013**, *15*, 1114-1124.
- (9) Newbloom, G. M.; de la Iglesia, P.; Pozzo, L. D., *Soft Matter* **2014**, *10*, 8945-8954.
- (10) Blouin, N.; Michaud, A.; Leclerc, M., *Adv. Mater.* **2007**, *19*, 2295-2300.
- (11) Beaupré, S.; Leclerc, M., *J. Mater. Chem. A* **2013**, *1*, 11097-11105.
- (12) Wang, H.-W.; Pentzer, E.; Emrick, T.; Russell, T. P., *ACS Macro Lett.* **2013**, *3*, 30-34.
- (13) Blouin, N.; Michaud, A.; Gendron, D.; Wakim, S.; Blair, E.; Neagu-Plesu, R.; Belletête, M.; Durocher, G.; Tao, Y.; Leclerc, M., *J. Am. Chem. Soc.* **2008**, *130*, 732-742.
- (14) Park, S. H.; Roy, A.; Beaupré, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J., *Nat. Photonics* **2009**, *3*, 297-302.

- (15) Peters, C. H.; Sachs-Quintana, I. T.; Kastrop, J. P.; Beaupré, S.; Leclerc, M.; McGehee, M. D., *Adv. Energy Mater.* **2011**, *1*, 491-494.
- (16) Clulow, A. J.; Tao, C.; Lee, K. H.; Velusamy, M.; McEwan, J. A.; Shaw, P. E.; Yamada, N. L.; James, M.; Burn, P. L.; Gentle, I. R.; Meredith, P., *Langmuir* **2014**, *30*, 11474-11484.
- (17) Gilbert, E. P.; Schulz, J. C.; Noakes, T. J., *Physica B* **2006**, 385–386, *Part 2*, 1180-1182.
- (18) Kline, S., *J. Appl. Crystallogr.* **2006**, *39*, 895-900.
- (19) Kasaai, M. R.; Charlet, G.; Arul, J., *Food Res. Int.* **2000**, *33*, 63-67.
- (20) Durand, A., *Eur. Polym. J.* **2007**, *43*, 1744-1753.
- (21) Macosko, C. W., *Rheology: Principles, Measurements and Applications*. First ed.; John Wiley & Sons, Inc.: New York, **1994**, 481-482.
- (22) Sperling, L. H., *Introduction to Physical Polymer Science*. Fourth ed.; John Wiley & Sons, Inc.: Hoboken, New Jersey, **2006**, 112-117.
- (23) Clulow, A. J.; Armin, A.; Lee, K. H.; Pandey, A. K.; Tao, C.; Velusamy, M.; James, M.; Nelson, A.; Burn, P. L.; Gentle, I. R.; Meredith, P., *Langmuir* **2014**, *30*, 1410-1415.
- (24) Calculated from the reported density of 1,2-dichlorobenzene in the *CRC Handbook of Chemistry and Physics*, Ninety-sixth ed., accessed online.
- (25) Hammouda, B.; Ho, D. L.; Kline, S., *Macromolecules* **2004**, *37*, 6932-6937.
- (26) Hammouda, B.; Horkay, F.; Becker, M. L., *Macromolecules* **2005**, *38*, 2019-2021.
- (27) Hammouda, B., *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 3195-3199.
- (28) Hammouda, B., *Polymer* **2009**, *50*, 5293-5297.
- (29) de Gennes, P.-G., *Scaling Concepts in Polymer Physics*. First ed.; Cornell University Press: Ithaca, New York, **1979**, 113-123.

Table of Contents Graphic

For table of contents use only

Clustering of high molecular weight PCDTBT in bulk-heterojunction casting solutions

Andrew J. Clulow,^{*1} Elliot P. Gilbert,² Pascal Wolfer,¹ Paul L. Burn^{*1} and Ian R. Gentle¹

