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Solubility of P3HT in chloroform and chloroform:acetone mixtures: A spin-echo SANS study

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ABSTRACT

P3HT is a semiconducting polymer widely used in solution-processable photovoltaic research. Measuring the solubility of P3HT in organic solvents is usually an arduous and time-consuming process. Here we report the presence or absence of P3HT nanoparticle agglomeration in optically opaque solutions of P3HT, with concentrations ranging from 6.2 to 22.0 mg·mL^{-1}, in pure chloroform and in chloroform:acetone mixtures, using the neutron scattering technique, Spin-Echo Small Angle Neutron Scattering (SESANS). We demonstrate *in-situ* that the solubility of P3HT decreases from ~ 22.0 mg/mL to < 6.2 mg/mL when the amount of acetone in solution increases from 0 vol% to 60 vol%. This work uses the ability of SESANS to probe P3HT nanoparticle aggregates, with dimensions ranging from ~ 1 to several microns, in P3HT solutions with concentrations above the solubility limit.

1. Introduction

Poly(3-hexylthiophene-2,5-diyl) (P3HT) is a benchmark semiconducting polymer widely used in organic photovoltaics research. Its use relies on solution-processing methods such as spin-coating because, contrary to commodity polymers, P3HT cannot be melt-processed, as it degrades before melting [1]. Furthermore, the processing of P3HT is difficult to implement using other solventless methods [2]. Therefore, the solubility of P3HT in different solvents is a topic of general interest among the organic photovoltaics research community [3,4]. However, measuring the solubility of semi-conducting polymers such as P3HT in different solvents is usually a cumbersome, tedious and time-consuming process that involves the following steps [3,4]: (i) measuring the UV–Vis spectra of solutions with low concentration and drawing calibration curves; (ii) preparation of saturated solutions and their filtration to remove undissolved solid material; (iii) dilution of filtered saturated solutions with solvent to attain an optical density within the calibration curve range; (iv) determination of saturation concentration value by multiplying the diluted concentration with the dilution factor used.

Spin-Echo Small Angle Neutron Scattering (SESANS) has been recently used in several areas of materials science, namely for instance in the study of fullerene agglomerates [5], food science [6], polymer composites [7] and colloids [8]. Here, we report the use of SESANS to study the solubility limits of P3HT in pure chloroform and chloroform: acetone mixtures. We have already shown that SESANS is a powerful method to determine *in-situ* the presence or absence of semi-conducting agglomerates in optically opaque solutions of PCBM [5], we now demonstrate that it can be applied more generally, by investigating a system containing P3HT. SESANS allows the determination of solubility limits without the need for the processes of filtration/centrifugation and dilution to the optical density as discussed above.

2. Materials and methods

Regioregular P3HT, with Mw = 24,480, Mn = 8,750, PDI = 2.8 and 93.6 % RR, was purchased from Ossila (code: M107). Chloroform D ($CDCl_3$ with 99.8 %D) and acetone-d_6 (CD_3COCD_3 with 99.8 %D) were purchased from Eurisotop.

Sample solutions (2 mL) of P3HT with concentrations 6.2, 12.8, 17.0 and 22.0 mg·mL^{-1} were prepared in four different solvent mixtures of chloroform-d/acetone-d_6 with volume fractions 100:0 (pure chloroform-d), 80:20, 60:40 and 40:60. During solution preparation, appropriate amounts of P3HT were weighed and added to appropriate amounts of pure chloroform-d in amber glass vials with 5 mL volume

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and screw cap. The solutions were stirred vigorously in a hot plate at 50 °C for 30 min, to dissolve the P3HT. Then appropriate volumes of acetone-d_6 were added to each glass vial and the solutions were stirred vigorously for an additional 30 min. After cooling down to room temperature the solutions were transferred into disc-shaped "banjo" quartz cells with a 2 mm path-length and an approximate volume of 1.5 mL and these were transferred into the beamline. SESANS measurements were performed on the Larmor beamline at the ISIS pulsed neutron and muon source. As per our earlier work [5], samples in quartz cells were subsequently mounted on a non-magnetic rotator. This serves to prevent sedimentation of the sample, the rotation speed was ~ 6RPM. The Larmor configuration used has RF flippers operated at a RF frequency of 2 MHz with the pole shoe angle being either −65 or −40 degrees. These parameters along with the neutron wavelength used defines the accessible length scale [9].

The spin echo length is calibrated using a one-micron silicon grating. This agrees well with the theoretical values for given magnetic field configurations. Data measured neutron polarisation (P) was corrected for the instrumental polarisation (P_0), neutron wavelength (λ) and thickness (t) to arrive at the reduced SESANS signal ($\ln(P)/(\lambda^2 t)$). This data was subsequently analysed using SasView [10]. As in our earlier work this provides two pieces of information, one is a correlation function and secondly a measure of the total amount of scattering. PCBM agglomerates in solution can be well described by a randomly distributed two phase DAB model [5,11,12], as we showed previously. This model gives a characteristic length scale of the agglomerates and a measure of the scattering. This measure of the scattering can be converted into a volume fraction of the agglomerates [5]. We derive the P3HT solubility as the maximum P3HT concentration before agglomerates start to be detected in solution.

3. Results and discussion

The scattering results obtained are shown in Fig. 1. While some solutions scatter strongly (e.g. 17 mg.mL^{-1} in a chloroform-d:acetone-d_6 40:60 mixture); others scatter weakly (e.g. 6.2 mg.mL^{-1} in a chloroform-d:acetone-d_6 40:60 mixture) and others do no scatter at all (e.g. 6.2 mg.mL^{-1} in a chloroform-d:acetone-d_6 60:40 mixture).

Table 1 and Fig. 2 summarize the main observations and conclusions from the scattering data. In pure chloroform-d (0 % acetone-d_6),

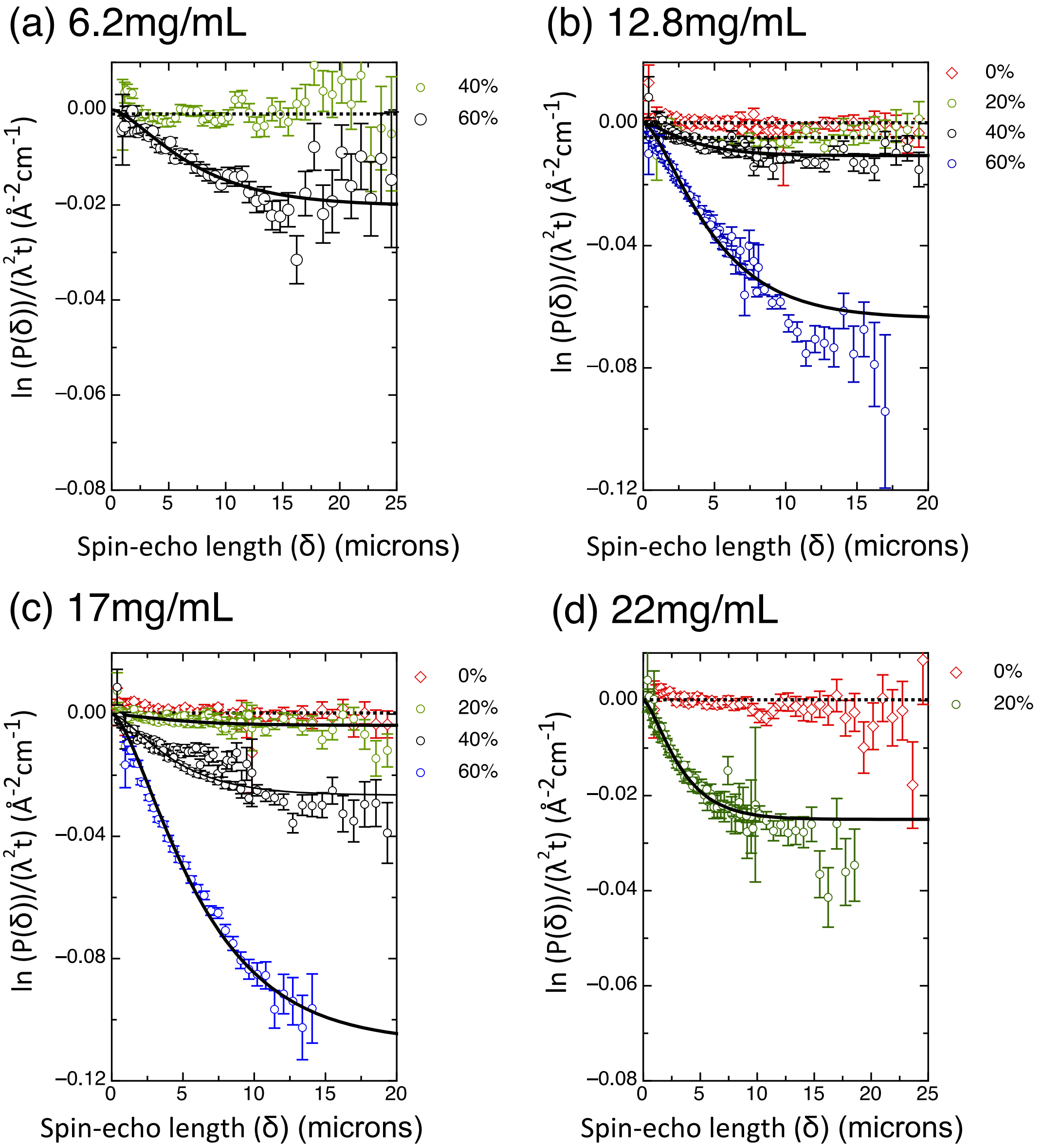

Fig. 1. Scattering as a function of spin-echo length for P3HT in chloroform-d:acetone-d_6 ($CDCl_3$:CD_3COCD_3) mixtures. Note the volume fraction of acetone-d_6 in the legend. Fits (solid line) using the DAB model, whereas the dashed line indicates a measure of the degree of scattering.

Table 1
Summary of fit parameters obtained from the SESANS data. Note that a DAB model is assumed unless indicated by* which denotes a linear fit as explained in the text (note that in the latter only a linear fit is applied and only Σ_t/λ^2 is fitted).

Polymer fraction (mg/mL)	Acetone %v	$\Sigma_t/\lambda^2(\text{Å}^{-2})$	ϕ_{P3HT} (aggl.)	DAB correlation length (μm)	Below or above the Solubility limit?
6.2	0	–		–	Below[a]
	20	–		–	Below[a]
	40	$2 \times 10^{-4} \pm 5 \times 10^{-4}$ *	$\mathbf{4 \times 10^{-5}}$	–	Below
	60	$2.0 \times 10^{-2} \pm 1.3 \times 10^{-3}$	$\mathbf{4 \times 10^{-4}}$	4.8 ± 0.4	Above
12.8	0	$2.1 \times 10^{-4} \pm 3 \times 10^{-4}$ *	$\mathbf{2 \times 10^{-4}}$	–	Below
	20	$4.6 \times 10^{-3} \pm 2 \times 10^{-4}$ *	$\mathbf{4 \times 10^{-3}}$	–	Below
	40	$1.0 \times 10^{-2} \pm 4 \times 10^{-4}$	$\mathbf{5 \times 10^{-3}}$	2.3 ± 0.4	Above
	60	$6.4 \times 10^{-2} \pm 1 \times 10^{-3}$	$\mathbf{3 \times 10^{-2}}$	3.3 ± 0.1	Above
17.0	0	$3.6 \times 10^{-4} \pm 1 \times 10^{-4}$ *	$\mathbf{2 \times 10^{-4}}$	–	Below
	20	$3.7 \times 10^{-3} \pm 6 \times 10^{-3}$	$\mathbf{2 \times 10^{-3}}$	3.1 ± 0.6	Above
	40	$2.7 \times 10^{-2} \pm 7 \times 10^{-4}$	$\mathbf{1.5 \times 10^{-2}}$	3.0 ± 0.1	Above
	60	$0.11 \pm 3 \times 10^{-3}$	$\mathbf{3 \times 10^{-2}}$	4.2 ± 0.02	Above
22.0	0	$1.5 \times 10^{-4} \pm 2 \times 10^{-4}$ *	$\mathbf{1.5 \times 10^{-4}}$	–	
	20	$2.5 \times 10^{-2} \pm 1 \times 10^{-3}$	$\mathbf{3 \times 10^{-2}}$	2.2 ± 0.01	Above
	40	–		–	Above[a]
	60	–		–	Above[a]

[a] Experiment not performed but result can be assumed based on the other experimental results.

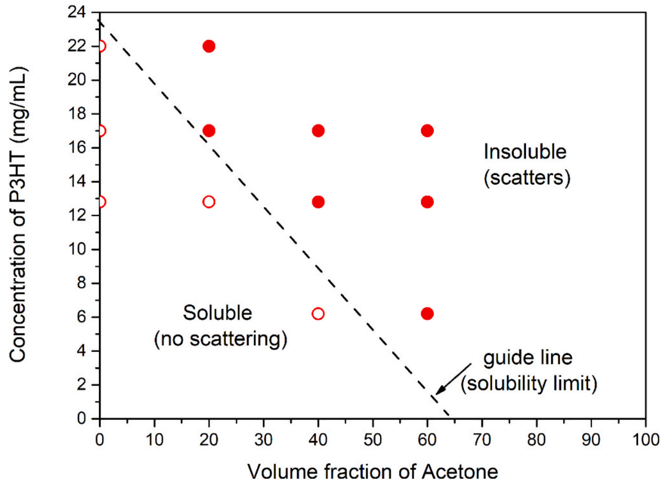

Fig. 2. Summary of experimental results and conclusions. Closed circles represent solutions containing P3HT agglomerates that scatter neutrons and open circles represent solutions that either do not contain P3HT agglomerates or contain in quantities below the detection limit of the technique. A dashed solubility limit guideline is also represented.

solutions with P3HT concentrations of 6.2, 12.0, 17.0 and 22.0 mg/mL do not scatter indicating that the P3HT is either completely dissolved or the amount of undissolved P3HT is small and below the detection limit of the technique. We note that the solubility of P3HT depends on its molecular weight M_w and according to literature the solubility of P3HT in chloroform may vary from ~ 38 mg/mL ($M_w = 19000$) [3] to ~ 14 mg/mL ($M_w = 65600$) [4]. In the present work, the P3HT has a $M_w = 24480$, intermediate between those two in the literature and as expected, its solubility in pure chloroform is also intermediate between 14 and 38 mg/mL. Acetone is a non-solvent for P3HT, being the solubility of P3HT in acetone ~ 4×10^{-4}mg/mL [3]. Therefore, when the amount of acetone in a chloroform: acetone solution increases, the overall solubility of P3HT is expected to decrease, which is what is observed. For example, the solubility of P3HT in a solution with 20 vol% acetone is between 12.8 and 17.0 mg/mL, whilst the solubility of P3HT in a solution with 40 vol% acetone is between 6.2 and 12.8 mg/mL. Similar observations were previously made by Machui et al. [4] in a study of P3HT solubility using the standard calibration curve method, combined with a binary solvent gradient method.

In this work we have not considered the effect of P3HT molecular weight on the solubility limit as represented by the dashed line in Fig. 2. Interestingly, Spann et al. [13] recently observed that the conjugation lengths of higher molecular weight P3HT are more sensitive to the solvent quality. Therefore, it is our expectation that an increase in the M_w of P3HT will not only shift the guideline in Fig. 2 down towards lower P3HT concentrations, but it will also increase its steepness, i.e. the solubility will become more dependent on the solvent quality.

The results obtained here can be also qualitatively explained using Hansen solubility parameters (HSP). P3HT has the following HSP: $\delta_D = 18.5$, $\delta_P = 5.3$ and $\delta_H = 5.3$ MPa$^{1/2}$ [14]. Chloroform has the HSP [15]: $\delta_D = 17.8$, $\delta_P = 3.1$ and $\delta_H = 5.7$ MPa$^{1/2}$. Acetone has the HSP [15]: $\delta_D = 15.5$, $\delta_P = 10.4$ and $\delta_H = 7.0$ MPa$^{1/2}$. Therefore, acetone is much more polar than both chloroform and P3HT and the addition of acetone to chloroform results in an increase of the polar part in the HSP of the solvent mixture which is the main responsible for the reduction in solubility of P3HT.

4. Conclusions

In conclusion, SESANS has been used to study the agglomeration behaviour of P3HT in pure chloroform and in chloroform:acetone mixtures. Using a simple and fast method we demonstrate in-situ that the solubility of P3HT decreases from ~ 22.0 mg/mL to < 6.2 mg/mL when the amount of acetone in solution increases from 0 vol% to 60 vol%.

CRediT authorship contribution statement

Gabriel Bernardo: Writing – review & editing, Writing – original draft, Resources, Methodology, Investigation, Formal analysis, Conceptualization. **Adélio Mendes:** Writing – review & editing, Writing – original draft, Resources, Funding acquisition. **Steven R. Parnell:** Writing – review & editing, Writing – original draft, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Steven Parnell reports equipment, drugs, or supplies was provided by Science and Technology Facilities Council. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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