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Determination of the P3HT:PCBM solubility parameters via a binary solvent gradient method: Impact of solubility on the photovoltaic performance

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ABSTRACT

We discuss an alternative route to determine the solubility parameters of two prototype organic semiconductors, namely the semi-crystalline polymer poly-(3-hexylthiophene-2,5-diyl) (P3HT) and the methano-fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM). The HSP (Hansen solubility Parameters) derived by this novel method are compared to the findings derived from the classical multi-solvent method to determine the HSP, and significantly higher accuracy is found. For this novel approach we designed two component solvent blend systems, being composed by mixing a solvent with a non-solvent. Varying the composition of the solvent – non-solvent blends from 0% to 100% gradually converts a solvent into a non-solvent. This very accurate control of the dispersive, polar and hydrogen contributions to the overall solubility now allows determining the Hansen sphere for P3HT and PCBM with much higher accuracy. The transition from a solvent into a non-solvent was further followed by solar cell investigations. Comparing the solubility studies with device investigations allows identifying the processing limits of solvent systems.

1. Introduction

The need for inexpensive renewable energy sources continues to encourage new approaches for efficient, low-cost photovoltaic devices. Solution-processed organic photovoltaics (OPV) have gained great research interest during the last few years and are slowly establishing themselves as one of the promising low-cost photovoltaic technologies. [1] Significant advancements in the design and synthesis of novel semiconductors have led to certified efficiencies of 8.3% and most recently to 10%. [2–4] Currently the commonly most used concept for the active layer is the bulk heterojunction, which consists of an interpenetrating network of a hole donating and an electron accepting semiconductor couple, thus exhibiting an increased interface for charge generation as compared to a bilayer approach. By spontaneous phase separation during film formation an intimate mixture of two nanostructures is formed which is decisive for the charge generation as well as for the charge transport. Poly-(3-hexylthiophene-2,5-diyl) (P3HT) a conjugated semi-crystalline organic semiconductor and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) a fullerene derivative are currently the two most prominent prototype semiconductors used for the OPV development. [5]

The biggest interest in organic photovoltaics stems from its compatibility to printing and coating processes. However, in order to fully exploit the capacity and the potential of the currently proposed high volume / high throughput solution based production processes, a careful design of the inks is mandatory. A proper ink design for multi-component formulations needs to respect several quite interdisciplinary design objectives: (i) sufficient solubility to dissolve the individual components, (ii) a careful design of the rheological properties as well as the ink's surface energy, (iii) suitable drying kinetics and finally, most decisive (iv) the built-in ability to form the right microstructure. Besides the pure technical design criteria, soft facts like non-hazardous solvent systems, recycling of a positive life cycle analysis balance are further decision criteria. By today, halogenated solvents, like chlorobenzene, o-dichlorobenzene or chloroform are the standard solvent systems for lab processing due to their excellent solubility for conjugated polymers and molecules. However, the toxicity of these solvents will not allow to proceed to mass production in industrial countries with a strict environmental, health and safety (EHS) legislation.

Besides the need for green solvents, the structure – property correlation between the ink formulation and the resulting solid state microstructure is of outmost interest. Due to the phase formation during the drying process, the choice of the processing solvent has a major impact on the resulting microstructure and thus on the solar cell performance. Shaheen et al. were among the

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first to demonstrate the importance of solubility. [6] By changing the solvent system from toluene and chlorobenzene, they were able to demonstrate a threefold better device performance for chlorobenzene over toluene, as a clear result of the improved solubility of both semiconductor components in chlorobenzene.

The design of ink formulations does offer further opportunities to control the film morphology: One method is the use of solvent blends or additives in organic photovoltaics, which offers the possibility of tailoring the solubility of individual components in binary or ternary systems. Advantages of these methods are the easy application to polymers with high as well as low solubility without further additional post-processing. The most prominent example for the use of additives was recently reported by Peet et al., who originally used dithieno-octanes to coarsen the morphology of too intimate mixed composites of P3HT and PCBM and later applied the same strategy to improve the performance of a small band gap polymer bridged bithiophene poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) in combination with [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) solar cells. [7] A second, evenly attractive approach is the addition of small amounts of non-solvents to good solvents was also shown to cause enhanced phase separation in the case of P3HT:PCBM solar cells. [8]

As mentioned above, the design of ink formulations does require a multi-parameter optimization routine. The most important input parameter for this routine is the knowledge of the solubility of the individual semiconductors. By today, there is no established method in the field of organic electronics for the determination of the absolute solubility as well as the solubility parameters. Analyzing the solubility of organic semiconductors is therefore the first step into the journey towards formulation of highly efficient semiconductor inks for organic solar cell applications.

It is the purpose of this manuscript to introduce a novel method to determine the solubility parameters of conjugated semiconductors. This method is an expansion of the Hansen Solubility Parameter (HSP) theory.

Hansen solubility parameters (HSP) were recently suggested as a useful tool to describe and predict the solubility behavior of organic semiconductors. [9], [10] The concept of solubility parameters was introduced by Hildebrand and Scott, who defined the total Hildebrand parameter δ_T as the square root of the cohesion energy density according to Eqs. (1) and (2) with V as the molar volume and E as the total cohesion energy. The cohesion energy E is the sum of the evaporation enthalpy ΔH minus the inner energy of the solvent RT, with T as the absolute temperature and R as the global ideal gas constant. [11] Hansen later suggested to separate the Hildebrand parameter into at least three different contributions resulting from atomic dispersive interactions (δ_D), permanent dipole molecular interactions (δ_P) and molecular hydrogen bonding interactions (δ_H) (Eq. (3)). [12]

$$\delta_T = \sqrt{(E/V)} \tag{1}$$

$$E = \Delta H - RT \tag{2}$$

$$(\delta_T)^2 = (\delta_D)^2 + (\delta_P)^2 + (\delta_H)^2 \tag{3}$$

Solubility properties are usually plotted in a three-dimensional coordinate system with the three Hansen parameters as the x, y and z axis. HSP coordinates of a solute are determined by analyzing the solubility of this solute in a series of solvents with known Hansen parameters. Fitting a spheroid into the solubility space identifies the solubility volume of this solute. The solubility volume of a solute is defined by a spheroid, with the center of the sphere being the three Hansen parameters and the radius of the sphere R_0 spanning the regime within which the solute is being dissolved.

Another important parameter is the solubility 'distance' parameter, R_a, reflecting the difference in respective partial solubility parameters between one solvent and one solute. R_a is defined via Eq. (4) with δ_{D2} as dispersive component for the solvent, δ_{D1} as dispersive component of the solute, where else δ_P and δ_H represent the polar part and the hydrogen bonding part respectively. Furthermore a, b, and c are used as weighting factors. Settings of $a=4$ and $b=c=1$ were suggested by Hansen based on empirical testing. Other weighting factors convert the Hansen spheroid into an ellipsoid. Taking these weighting factors into account converts the otherwise ellipsoidal body into a sphere, as seen by Eq. (4). [12]

$$(R_a)^2 = a(\delta_{D2}-\delta_{D1})^2 + b(\delta_{P2}-\delta_{P1})^2 + c(\delta_{H2}-\delta_{H1})^2 \tag{4}$$

HSP was already successfully applied to different material systems like polymer / multi-walled carbon nanotube composites, napthenic mineral oils, negative electron beam resists (e.g. hexamethyl acetoxy calyx(6)arene) and unfilled and filled polysiloxane-type preceramic polymer coatings. [13–16] Furthermore, Ruoff et al. analyzed the solubility of pure C_{60} with HSP. [17] Categorizing the various solvents according to their chemical structure helped to identify good solvent classes for fullerenes. In the first study on conjugated polymer / fullerene bulk heterojunction solar cells the limited solubility of pure C_{60} in organic solvents and the tendency to crystallize during film formation was recognized by members of the Heeger group. [18] By the use of soluble C_{60} derivatives like PCBM homogeneous stable blends with more than 80 wt.-% fullerene content became available. Kronholm and Hummelen published solubility values for PCBM in different aromatic solvents. [19] Troshin et al. analyzed the solubility of different fullerene derivatives and compared them to the resulting device performance. [20] For organic semiconductors HSP was used when Hansen and Smith analyzed pristine C_{60} in organic solvents and polymers. [21] Interestingly, even at that time it was concluded that good solvents for C_{60} would be polymers with the same functional groups. Furthermore, the temperature dependent solubility regimes have been investigated for P3HT, PCBM and a small band gap polymer, namely PCPDTBT (bridged bithiophene poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1- b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)]). [10] For the dominantly amorphous polymer PCPDTBT and the fullerene PCBM it was found that the HSP analysis gives consistent results over a broad temperature regime. A different observation was made for P3HT: due to the semi-crystalline character of P3HT an exact determination of the solubility parameters in a temperature regime between 25–140 °C was found difficult and showed some inconsistencies. The reason for this inconsistency was explained by the breaking of polymer aggregates (micro crystallites), which is a strongly temperature activated process.

Walker et al. analyzed a conjugated polymer 3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4–c]-pyrrole-1,4-dione (DPP(TBFu)2) and $PC_{71}BM$. [9] The solvents used in their study were classified in different categories according to their solubility. It was concluded that a combination of the processing solvents and thermal annealing could be used to control the film morphology and the degree of phase separation. Park et al. showed that using non-halogenated solvent blends with the same Hansen parameters as o-dichlorobenzene (o-DCB) could be used to reach comparable device performance. [22] They mixed mesitylene with acetophenone in different ratios to match the Hansen parameters of o-DCB. This has so far been the first HSP guided design of solvent blends for organic semiconductors and demonstrated the potential of the HSP method.