Viscosity control of Light-Emitting Polymer Inks for Large Area OLED Processing

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The Holst consortium has worked for four years now on lab- and pilot scale production of flexible organic light-emitting diodes (OLEDs) for lighting and signage applications using wet-deposition methodologies, such as inkjet printing[1], gravure printing[2], and slot coating[3]. The specifications regarding deposition stability and drying kinetics are very demanding to guarantee reliable production of devices having a homogeneous light output, high efficiency, and long life time. Due to the strict processing demands, light-emitting polymer (LEP) ink formulation can be a challenging and practically cumbersome task. Unfortunately, the formulation of suitable LEP-based ink systems is still largely based on time-consuming trial-and-error experimentation. Although high-throughput screening has shown to be a helpful tool for decreasing experimentation time for ink development,[4] not much physical insight is gained. The general preference for trial-and-error experimentation is hardly surprising, as the stability of a printing or coating process relies on a sensitive balance between many parameters, relating to processing conditions (*e.g.* shear rate, temperature, pressure, substrate characteristics) and ink properties (*e.g.* surface tension, viscosity, rheology, chemistry).

In order to speed up development, we focus on the construction of readily applicable models which assist ink formulation and process optimization by a priori estimation of physical properties of organic semiconductor solutions.[2a] We aim as much as possible for finding a

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compromise between obtaining fundamental understanding, predictive ability, and practicality.
A very important ink parameter is the dynamic viscosity, as it largely determines the compatibility with the deposition method. The viscosity of dilute to semi-dilute polymer solutions may be typically predicted via estimation of the intrinsic viscosity from the polymer molecular weight, in combination with tabulated values for the Mark-Houwink parameters and the Huggins constant. These data are available for numerous systems based on conventional polymers and solvents.[5] Estimates of the dynamic solution viscosity are then obtained using the Huggins equation, once the viscosity of the pure solvent is known. LEPs, however, usually have rather complicated conjugated back bone structures, often consisting of various co-monomers and charge transfer dyes. What's more, optimization of the printing and drying characteristics of LEP-based inks usually requires mixtures of two or more solvents for which viscosimetric data is generally not available.

For this reason we developed a powerful method which predicts LEP ink viscosity for a wide range of solvents and solvent combinations, based on only a few benchmark measurements. This novel approach combines group contribution theory, solution state analysis, and viscosimetry. The model, based on the estimation of the intrinsic viscosity and the Huggins constant as a function of solvency, allows accurate prediction LEP ink viscosity up to concentrations exceeding the overlap concentration. The model also gives a first order estimate of fluid elasticity, as well as viscosity changes during the initial stages of drying.

First, we determined the disperse (δ_d), polar (δ_p) and H-bonding (δ_H) contributions to the solubility parameter (δ_t) for polymer and solvent using the group contribution method of Hoy.[6] The solubility distance $\Delta\delta$, *i.e.* a measure for the interaction between solvent and solute, was determined via:

$$\Delta\delta = \sqrt{\left(\delta_{d,solvent} - \delta_{d,polymer}\right)^2 + \left(\delta_{p,solvent} - \delta_{p,polymer}\right)^2 + \left(\delta_{H,solvent} - \delta_{H,polymer}\right)^2} \qquad (1)$$

In case of solvent mixtures and (random) co-polymers, we used the mole-fraction weighted average of the solubility parameters of the pure components or monomers. As the degree of polymer chain solvation is one of the factors (together with the degree of polymerization, chain rigidity, and excluded volume) determining the intrinsic viscosity $[\eta]$ and the Huggins constant k, $\Delta\delta$ is related to the dynamic viscosity of the solution. We measured the viscosity as a function of concentration for a few solvents spanning the soluble range of $\Delta\delta$, after which we fitted the data to the extended Huggins equation, using $[\eta]$ and k as fitting parameters. In this equation the specific viscosity (η_{sp}) is related to the polymer concentration (c), as well as to $[\eta]$ and k. Higher order terms in the Huggins equation represent inter-chain interactions, relevant to concentrations exceeding the overlap concentration c^*.

In Figure 1 this fitting procedure is demonstrated for a poly(spirofluorene)-based LEP in tetralin. As shown by the inset, the required number of terms saturates. The values obtained for $[\eta]$ typically exceed values found for flexible polymers, indicating the effect of the semi-rigid nature, induced by the electronic conjugation of the LEP backbone.

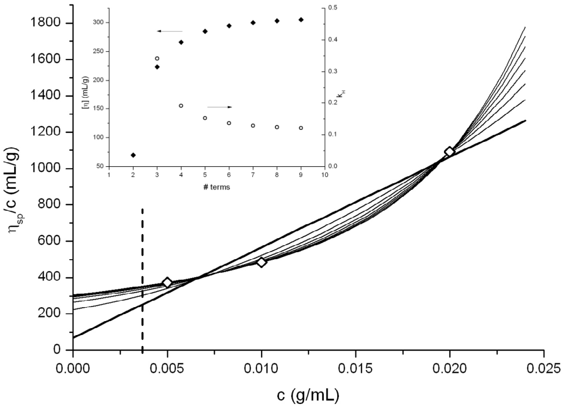

Figure 1. *η_{sp}/c plotted as a function of concentration for LEP in tetralin; the lines represent best fits using the extended Huggins equation corresponding to a cumulative number of terms; the inset represents the optimized fitting parameters [η] and k as a function of the number terms used during curve fitting (the values saturate at 300 mL/g and 0.12, respectively); the vertical dashed line marks the overlap concentration c*.*

Figure 2 shows [η] and *k* as a function of $\Delta\delta$ for two different molecular weights. The small, but significant, decreasing trend of [η] with $\Delta\delta$ expresses the decrease in coil dimension as a result of the drop in solvation of the polymer chains. The figure further suggests a slight increase in *k* with $\Delta\delta$.

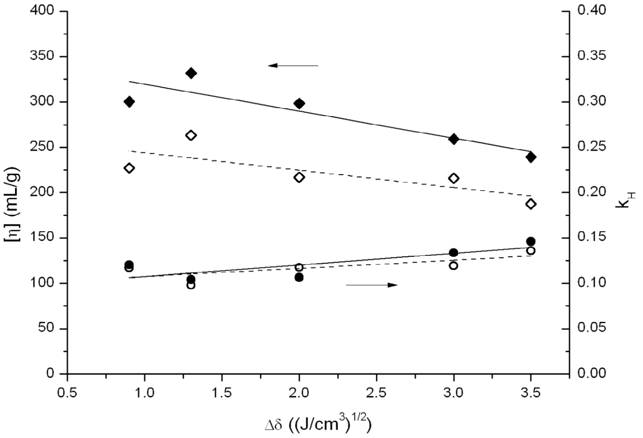

Figure 2. *[η] and k plotted as a function of $\Delta\delta$ for five different solvents; the closed and open symbols correspond to a low and a high molecular weight LEP, respectively; the solid and dashed lines represent empirical fits to first order polynomials.*

We fitted straight lines to the data plotted in Figure 2, yielding empirical calibration functions which can be substituted in the extended Huggins equation to give a direct relation between dynamic solution viscosity and $\Delta\delta$ for a chosen concentration range. Thus, we predicted the dynamic solution viscosity η of new solutions based on solvents and solvent mixtures that have not been included in prior measurements. The required viscosity of the solvent mixtures was calculated by any of the known methods described in [7]. Figure 3 shows calculated versus measured viscosity data of LEP solutions at various polymer concentrations for two different molecular weights. The prediction error is typically within 15%.

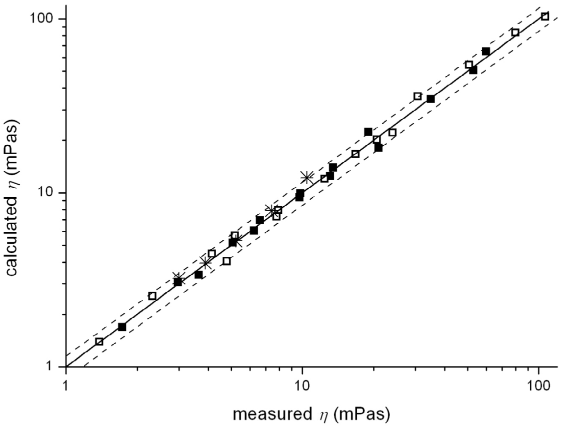

Figure 3. *Calculated solution viscosity versus measured values for poly(spirofluorene)-based LEP in various solvents and solvent combinations in the concentration range 0.005-0.03 g/mL; the solid line represents zero prediction error; the dashed lines indicate the 15% accuracy interval.*

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