

Printing PPEs: Fundamental Structure–Property Relationships

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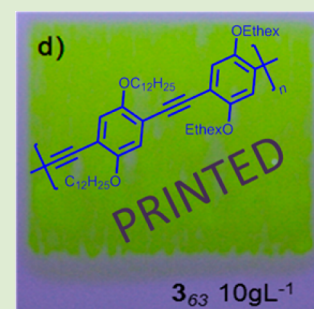
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S Supporting Information

ABSTRACT: A series of differentially alkyl- and alkoxy-substituted poly(*para*-phenyleneethynylene)s of different molecular weight were prepared and their rheological properties investigated. It was found that the side chain structure of the PPEs of roughly equal molecular weight and degree of polymerization has a significant influence on the rheology and printing behavior of the PPEs. Introduction of branched alkoxy or alkyl substituents improve the printing behavior of the PPEs dramatically.



High-throughput printing and coating of electronic functional polymers/materials is critically important for the development of cost efficient processing for organic electronics. The application of printed organic electronics using roll-to-roll printing techniques, such as gravure printing, should allow the efficient production of organic light-emitting diodes (OLEDs), photovoltaics or integrated circuits, and so on.^{1,2} However, a difficult problem in this area is the availability of functional inks that combine the desired optoelectronic properties and suitable rheological and flow features that facilitate the fabrication of high performance devices by printing techniques. This problem hinders the direct transfer of knowledge between the material optimization stage at the laboratory scale and the real world industrial processes.^{3,4} Furthermore, there is no real systematic understanding as to how the intrinsic molecular structure of an organic electronic material is connected to its ability to act as the main ingredient of an organic semiconductor ink. To shed light on this fascinating problem, we prepared a series of poly(*para*-phenyleneethynylene)s **1–3**^{5,6} of different structures and with different molecular weights and investigated their solutions with respect to their rheological properties and their application in gravure printing processes. We find that the molecular weight (as expected), but also subtle changes in the side chain structures, leads to significant changes in PPEs' rheological behavior.

We have prepared the PPEs **1–3** (Figure 1) using a classical Pd-catalyzed coupling reaction of the Sonogashira type.⁶ Details are provided in the Supporting Information (SI). The different

molecular weights of PPE **1** were obtained by varying the monomer concentration, the reaction temperature and the solvent composition. Lower reaction temperatures lead to lower molecular weights in the polymerizations, due to a lower solubility of the oligomeric fragments during the reaction; more detailed information can be found in the synthetic procedures in the SI. Consequently, we have a small library of PPEs with different structures and different molecular weights. The PPE **1** is the standard PPE and was obtained in several different degrees of polymerization, with the last two samples coming from different batches. For PPEs **3** and **4**, P_n denotes only half of the phenyleneethynylene units that are in the backbone.

In the first experiment we measured the shear dependent viscosities of the PPE samples **1**, having different molecular weights each at a concentration of 10 g L⁻¹ in toluene (Figure 2). Viscosity as a function of shear rate was measured in the cone–plate geometry on a HAAKE MARS rheometer at 23 °C using a volume of 1 mL. The viscosity increases with the molecular weight, and only **1**₇₀ and **1**₁₇₆ display a viscosity of 10–100 mPa·s, which is typically expressed as the optimum viscosity range for gravure printing of graphical inks (η_{print}).⁷ Clearly, **1**₁₁ is of too low molecular weight to increase the viscosity (even for concentrations larger than 30 g L⁻¹). Gravure printing of functional fluids with viscosities below

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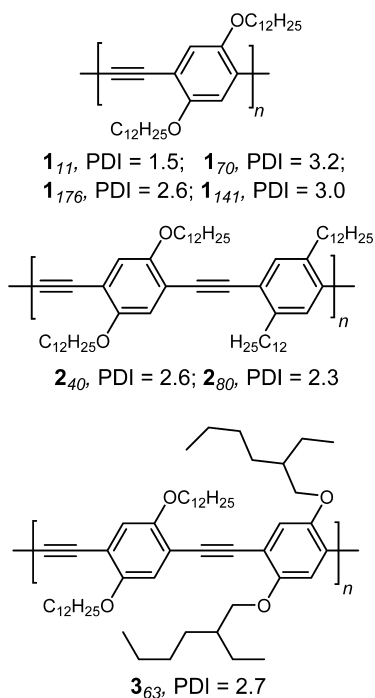


Figure 1. Structures 1–3 of the used PPEs. The subscripted and italicized numbers refer to the degree of polymerization (P_n). One should note that the repeat unit for 2 and 3 comprises two phenyleneethynylene units but for 1 of only one.

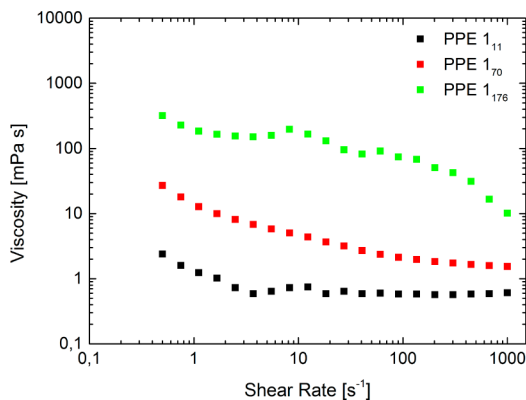


Figure 2. Viscosity vs shear rate for PPEs 1 at 10 g L^{-1} measured at 23°C : PPE $\mathbf{1}_{11}$ (black), $\mathbf{1}_{70}$ (red), and $\mathbf{1}_{176}$ (green).

$10 \text{ mPa}\cdot\text{s}$ is an ongoing field of research dedicated to the fabrication of functional films, homogeneous in the nanometer scale, that are suitable for device fabrication.^{8,9} Even though the viscosity magnitude of $\mathbf{1}_{70}$ and $\mathbf{1}_{176}$ is appropriate for gravure printing, both samples show significant shear thinning at higher shear rates, which would make them less ideal as functional inks since the non-Newtonian nature of the fluid favors hydrodynamical instabilities during the printing process.^{10,3} Moreover, it was observed that $\mathbf{1}_{70}$ and $\mathbf{1}_{176}$ gel at concentrations above 10 g L^{-1} and 5.4 g L^{-1} , respectively.

In the next experiment (Figure 3), we investigated the shear dependent viscosity of $\mathbf{1}_{176}$, $\mathbf{1}_{141}$, $\mathbf{2}_{80}$ and $\mathbf{3}_{63}$ at a concentration of 4 g L^{-1} . Here again for PPE 1 shear-induced thinning is observed. Even though the molecular weight of $\mathbf{1}_{176}$ is higher than that of $\mathbf{1}_{141}$, the flow curve of $\mathbf{1}_{141}$ lies above that of $\mathbf{1}_{176}$.

This was observed in repeated measurements and might be due to the different polydispersities of both samples. The PPEs

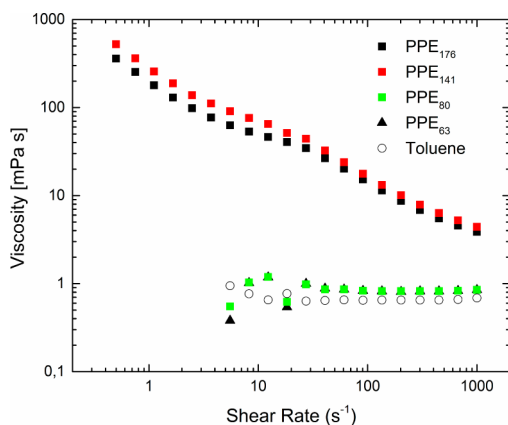


Figure 3. Viscosity vs shear rate for several different PPEs measured at 23°C . $\mathbf{1}_{176}$ (black), $\mathbf{1}_{141}$ (red), $\mathbf{2}_{80}$ (green), and $\mathbf{3}_{63}$ (blue) at concentrations of 4 g L^{-1} . Toluene (open circles) is shown as comparison.

2 and 3 of similar length show a dramatically different behavior. While long PPEs 1 gel at higher concentrations, 2 and 3 show Newtonian flow behavior over the whole shear range that was tested.

As we were very excited about this behavior, we examined the concentration dependent rheological behavior of 3. Figure 4

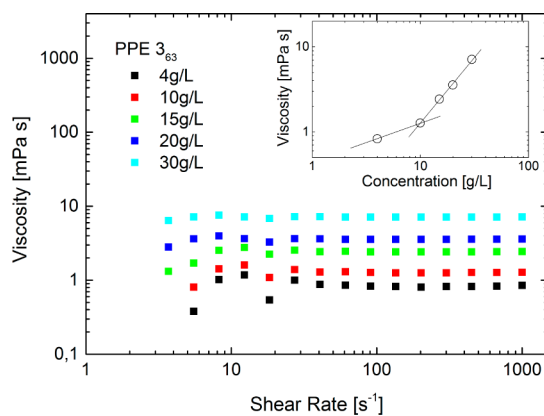


Figure 4. Viscosity vs shear rate for the PPE $\mathbf{3}_{63}$ at different concentrations (from 4 to 30 g L^{-1}) measured at 23°C . Note the almost shear-independent viscosity and the lack of gelling. Inset: Viscosity vs concentration at a shear rate of $100 \text{ mPa}\cdot\text{s}$.

shows that the Newtonian, shear independent viscosity behavior of 3 is concentration independent and that around 30 g L^{-1} one obtains PPE-solutions that should be ideal as gravure printing inks. Also, we note that there is no gelling of PPE 3 even at higher concentrations. In the inset, it can be observed that the viscosity increases as a power law after a critical concentration of 10 g L^{-1} due to an increased interaction between polymer chains.¹¹ Figure 5 shows actual printing experiments with PPEs 1–3, all at a concentration of 4 and 10 g L^{-1} . PPE 1 can only be used at lower concentration, due to the higher viscosity.

The samples were printed from a toluene solution at room temperature on poly(ethylene terephthalate) (PET) substrates using an RK gravure printing proofer with a field size of 2.24 cm^2 ($1.6 \times 1.4 \text{ cm}$) at a speed of $\sim 1 \text{ m s}^{-1}$. The cell volume per area of the gravure plate was 14 mL m^{-2} with 54 lines per cm. A detailed explanation of the gravure printing

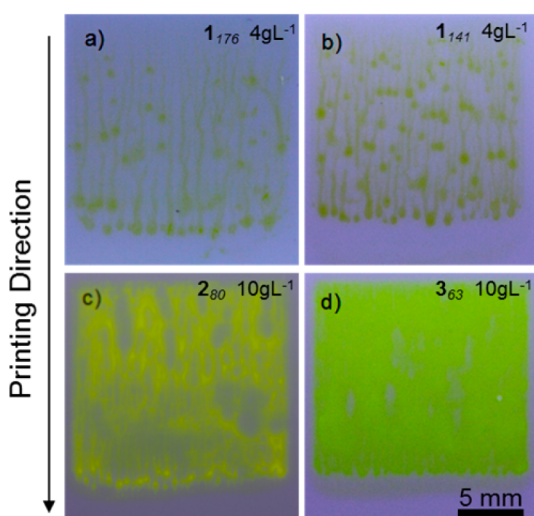


Figure 5. Contrast enhanced photographs of the printing fields under UV illumination. From (a) to (d) a significant improvement of the printing results, depending on the PPE structure, is observed.

process can be found in the SI. Visual inspection shows the dramatic improvement of the quality of the printed areas. While for **1** blotchy skeins with a tadpole-like appearance result, PPE **2** gives already better surface coverage. The exhibited texture in the printing direction of the films is known as “viscous fingering”. These film inhomogeneities are generated by hydrodynamic instabilities during the ink transfer from the gravure cells to the substrate and are accentuated by the non-Newtonian fluid behavior of the solution.¹² Surface tension of the functional inks was measured by the pendant drop method. Values between 24.4 and 27.9 mN m⁻¹ were obtained for the functional inks. This small difference in surface tension suggests that the wetting behavior of the inks to the PET substrate is very similar and that the printing outcome is mainly dependent on the flow properties of the fluids. The best printed samples are found from the dialkoxy-PPE **3**, which carries ethylhexyloxy-groups at every second benzene ring. Here we find even at suboptimal concentrations of 10 g L⁻¹ PPE well developed printed films.

In conclusion, we find that introduction of dodecyl chains or a branched ethylhexyloxy-chain into every second benzene ring results in nearly Newtonian flow curves in PPEs with a significantly lower viscosity at comparable molecular weight; a superb prerequisite for gravure printing. Surprisingly, subtle structural changes of PPEs’ side chains (!) have a dramatic impact on their fluid behavior and printability. Changes in molecular weight show less fundamental influence on the PPEs rheological and printing-related properties. PPEs **2** and **3** display structural features (branches, less oxygen atoms) more favorable for Newtonian behavior for the viscosity range needed for gravure printing.

As even very small changes in structure have such a significant effect on the runnability of the PPEs and a significant number of PPEs with very different structures are known, we will investigate structure–property relationships to find proper substituents that allow smooth printing. In addition, we will complement the work with a comprehensive morphological and optoelectronic characterization of the films. Once we have discovered the ideal substituent pattern, we will transfer these insights into the design of other semiconductor backbones such as PPVs and polythiophenes.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental section with preparation of PPEs and details of the printing and the rheological measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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