N-type semiconducting polymers a useful way for electron acceptors in polymer solar cells?

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The heterojunction organic photovoltaic cell consists of phase separated blends of typical hole- and electron-affine materials. Soluble poly(2,5-dialkoxy phenylenevinylene)s or poly-3-hexylthiophene are often used as light-absorbing and hole-transporting material. In the most successful cells fullerenes, especially the soluble PCBM, are used as electron-affine and –transporting material [1-3]. The charge separation takes place at the interphase polymer/fullerene.

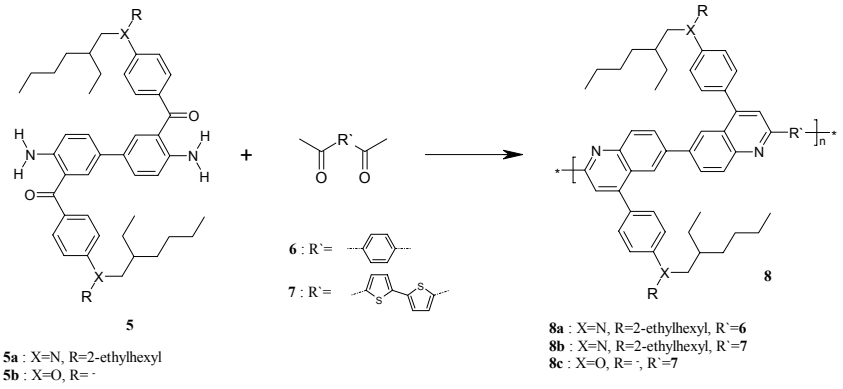
Such cells consist of up to 80 % p.w. of fullerene. The fullerene generates no remarkable contribution to the light harvesting of the cell. Therefore there is still a demand on strong electron-affine polymers which harvest light and overtake the outstanding function of the fullerene in such cell. The aim of this work is to develop some new organo-soluble polymer materials with typical n-type semiconducting properties and low reduction peak potentials.

Among these n-type materials N-heterocycle-containing polymers are some of the most favourable. The most common N-heterocycles used in such polymers are oxadiazoles because of their strong electron affinity. But also quinoxalines, pyridines and quinolines are incorporated into conjugated main chain polymers.

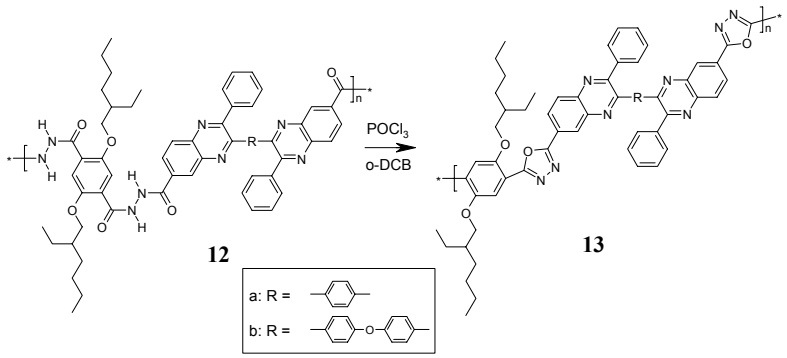
Often the application properties of these N-heterocycle main chain polymers are limited by their poor solubility in common organic solvents. Typical polyquinolines are only soluble in formic acid or as Lewis acid or aryl phosphate complexes. [4,5] The application of such dissatisfying solvents requires special conditions for film tempering and evaporating the solvent. It was our aim to develop new polyquinolines which are easily soluble in common organic solvents. Till now there are only very limited numbers of works available on organo-soluble polyquinolines. [6],[7]

We present the results on the synthesis and characterization of some new organo-soluble polyquinolines (PQ) and copolyquinoxalines (PQO). The electrochemical reduction and oxidation behavior of these polymers are studied by cyclovoltammetric measurements. The optical properties and the electrical characteristics of fully polymer solar cells made from blends of these new polymers with poly-[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenvinylen] (MEH-PPV) are described.

The substituted bis(o-aminophenylketone) monomers **5** were synthesized after a modified literature procedure [8]. The polymerisations were carried out in diphenylphosphate and m-cresol at 140 °C under argon (scheme 1).



Scheme 1: Polymerization of bis(o-aminophenylketones) with diacetyl monomers (diphenylphosphate, m-cresol)



The PQOs were synthesized by copolymerisation of quinoxaline precurser with bishydrazide forming a polyhydrazide **12** (scheme 2). The ring closure forming 3,4-oxadiazole heterocycles was catalysed by $POCl_3$ leading to the PQOs **13**.

Scheme 2: Synthesis of PQOs **13a** and **13b**

All the PQs and PQOs have good solubility in chloroform. The polymers show excellent film forming properties from chloroform solution. The absorption and photoluminescence of the polymers were measured in chloroform solution and in solid films. Quenching experiments were successful. The LUMO and HOMO values of the polymers were estimated by cyclovoltammetry. The lowest LUMO was found with –3,1 eV for PQO **13a**.

With this PQO and MEH-PPV first polymer blend cells were made and studied.

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