Communications to the Editor

Synthesis and Properties of a Soluble Conjugated Poly(azomethine) with High Molecular Weight

Olinga Thomas,[†] **Olle Inganäs,**[‡] **and**
Mats R. Andersson*[,†,§]

Departments of Organic Chemistry, and Polymer Technology, Chalmers University of Technology, S-41296 Göteborg, Sweden, and Department of Physics, IFM, Linköping University, S-58183 Linköping, Sweden

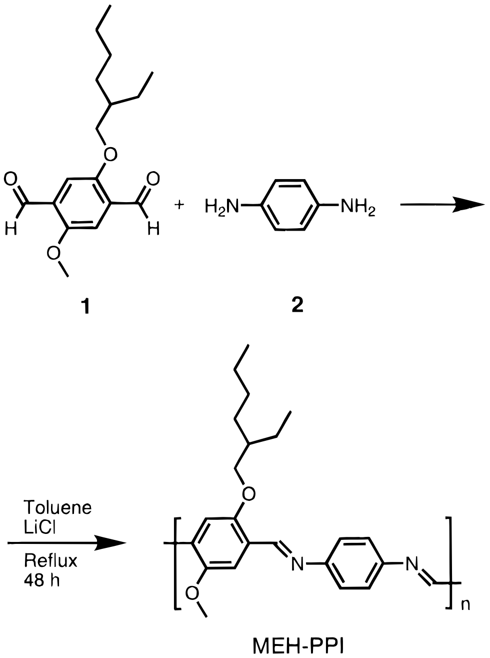
Received January 28, 1997
Revised Manuscript Received February 2, 1998

Functional polymers constitute a field of increasing scientific and technical interest, offering the potential for one to prepare a broad variety of promising materials with a wide range of optoelectronic properties. Conjugated aromatic poly(azomethines), or Schiff base polymers, have previously been synthesized, and their properties have been investigated.[1] For example, their synthesis, attractive thermal stability, good mechanical strength, meltability, and fiber-forming properties have been studied.[1] However, their insolubility in organic solvents limited their processing and made the understanding of their structures difficult. Strong protonic acids,[1] or Lewis acids in aprotic solvents,[2] were used to achieve processability and solubility of rigid chain polymers. This method gave interesting results in terms of structure and processing of these rigid polymers. Unfortunately degradation was observed after solubilization (in protonic acids) due to the hydrolysis of the azomethine linkage, leading to the breaking of polymer chains at random places.[1,3]

Another way to improve the solubility is to add flexible side chains onto the conjugated poly(azomethine) backbone.[4,5] Kwang-sup Lee et al.[4] have synthesized a series of *para*-linked aromatic poly(azomethines) with linear alkoxy side chains. All the polymers were soluble in organic solvents, but the molecular weight, $\bar{M}_w$, was limited to 10 000.[4] Sang-Bong Park et al.[5] have also prepared soluble poly(azomethines) but with linear (alkoxy)methyl side chains. They pointed out that the introduction of linear (alkoxy)methyl side chains with different lengths improve the solubility of these polymers, but only when the molecular weight is limited.

We report herein the synthesis, characterization and photostability of a *para*-linked aromatic poly(azomethine) with methoxy and 2-ethylhexyloxy side chains, namely MEH–PPI (Scheme 1). It is to be noted that the structure of MEH–PPI resembles that of poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene)[6] (MEH–PPV) which is highly soluble due to the branched side chain and the unsymmetrical substitution, giving random regioregularity.

Scheme 1. Synthesis and Structure of MEH–PPI



The motivation to prepare this polymer was its potential use in photonic devices as thin films spin-casted from solutions. Poly(azomethines), made by vapor deposition of the monomers in a vacuum chamber, have been used as electron transporting layers in polymer light-emitting diodes.[7,8]

The dialdehyde **1** was prepared as reported in the literature.[9] The polymer, MEH–PPI, was synthesized by polycondensation of the dialdehyde **1** with 1,4-phenylenediamine in anhydrous toluene and lithium chloride, which was used as a water-absorbing reagent. After 2 days of refluxing, an excess of 1,4-phenylenediamine was added to give amine end groups in order to avoid a further polycondensation reaction of the polymer chains. The polymer was precipitated into methanol, and after purification it was isolated as an orange powder. The polymer has high solubility in chloroform at room temperature. No “melting” point of MEH–PPI was detected below 250 °C, when it was examined with a melting point microscope.

The polymer structure was investigated by ^{1}H NMR and IR spectroscopy. The ^{1}H NMR spectrum displayed a signal at δ 9.03 which is attributed to the azomethine proton, as described earlier.[4] The presence of a single signal, in contrast with earlier results,[3,4] for the azomethine proton suggested the occurrence of only one isomer, which is presumably the thermodynamically more stable trans isomer. The signals due to the

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* To whom correspondence should be addressed.

[†] Department of Organic Chemistry, Chalmers University of Technology.

[‡] Linköping University.

[§] Department of Polymer Technology, Chalmers University of Technology.

S0024-9297(97)00109-5 CCC: $15.00

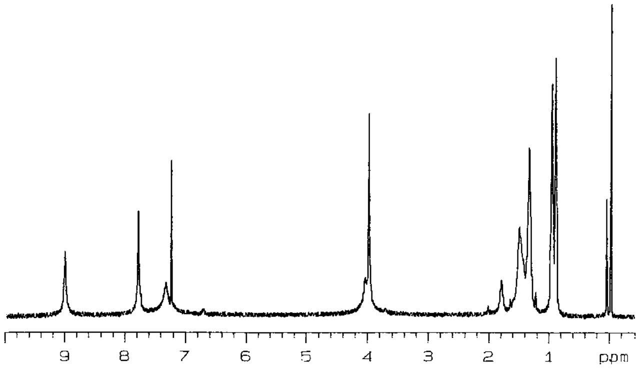

Figure 1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of MEH−PPI.

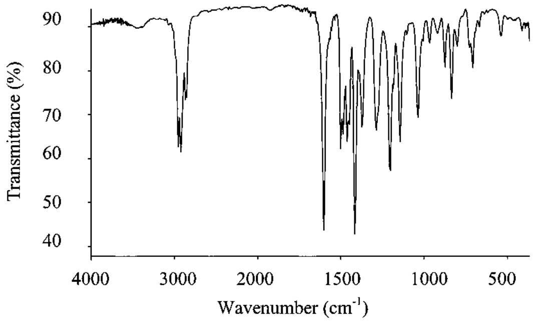

Figure 2. IR spectrum from a film of MEH−PPI on a KBr disk.

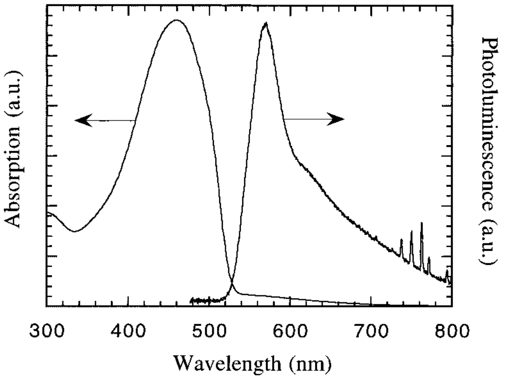

Figure 3. UV−vis absorption and emission spectra of a spin-coated film of MEH−PPI on glass.

aromatic protons appeared at δ 7.81 and 7.36. The broad doublet at δ 4.05 and the singlet at δ 4.00 are assigned to the methylene and methyl groups attached to the oxygens, respectively. The remaining aliphatic proton signals appeared at δ 1.83, 1.56, 1.36, 0.98, and 0.92 (Figure 1).

The IR spectrum showed a strong absorption band at 1604 cm^{-1}, assigned to the azomethine (C=N) stretching[3] (Figure 2). No clear signal for the amine end groups was detected above 3000 cm^{-1}.

Size exclusion chromatography (SEC) of this polymer in chloroform, using polystyrene standard for calibration, gave a molecular weight ($\bar{M}_w$) of 107 000 and a polydispersity of 4. This result is consistent with the IR and ^{1}H NMR results that no amine end groups could be detected. The UV−vis absorption maxima occurred at 465 nm, for the polymer dissolved in chloroform, and at 460 nm (2.70 eV) for spin-coated films on glass (Figure 3). The photoluminescence spectrum from spin-coated films showed a maximum at 570 nm when excited with a broad band UV lamp. MEH−PPI exhibited very poor photoluminescence efficiency both in solution and in the solid state.

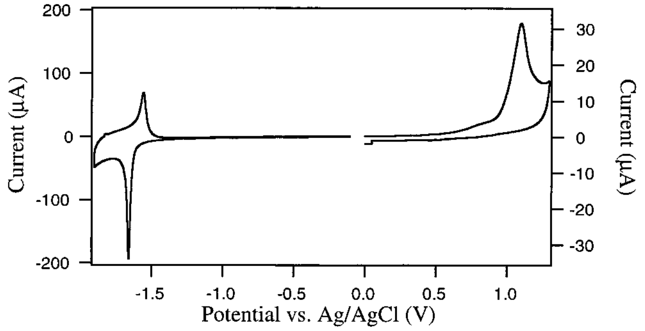

Figure 4. Cyclic voltammograms of two films of MEH−PPI on a Pt wire (0.08 M $(TBA)ClO_4$ in acetonitrile) at a scan rate of 100 mV/s.

MEH−PPI was adsorbed onto a Pt electrode and its cyclic voltammogram was recorded in 0.08 M tetrabutylammonium perchlorate ($(TBA)ClO_4$) in acetonitrile (Figure 4). The potential was calibrated with 1,1′-dimethylferrocene (0.19 V vs Ag/AgCl). Reversible reduction was observed with a peak at −1.66 V and a formal potential at −1.61 V vs Ag/AgCl. Irreversible oxidation with a peak at 1.10 V was also observed. These are roughly the same values as for a dimethoxy-substituted poly(azomethine) analogue to MEH−PPI.[10] Oxidation and reduction of MEH−PPI showed a rapid loss of electroactivity. From the formal potential of the reduction process, we could determine the LUMO position for MEH−PPI to be located at 3.1 eV, as the normal hydrogen electrode (NHE) is found at 4.5 eV[11] and that for Ag/AgCl is found at 0.22 V vs NHE. The HOMO position for MEH−PPI was calculated from the peak potential of the oxidation due to the irreversible oxidation and was found to be at 5.8 eV. The position of HOMO is in agreement with device characteristics of light-emitting diodes prepared from a poly(azomethine) analogue to MEH−PPI without substituents.[8] The band gap (HOMO−LUMO) of the polymer determined from the electrochemical data is 2.7 eV. This can be compared to the band gap determined optically, 2.70 eV, which is unusually close to the band gap determined electrochemically. The optical band gap was determined from the energy of the absorption maximum of the film, as expected for an ideal 1-D electronic system.[12]

The stability of MEH−PPI in the presence of light and air was also investigated. Spin-coated films of MEH−PPI and MEH−PPV on glass substrates were put into a Petri dish and exposed to light from a normal desk lamp in air. The disappearance of the $\pi-\pi^*$ transition of the films was followed by UV−vis spectroscopy. This study revealed that MEH−PPI was more stable than MEH−PPV. The degradation of the MEH−PPV film occurred at a much faster rate. In the spectra of the degraded MEH−PPI film, a new peak with low intensity appeared at longer wavelengths. No changes in absorption could be observed for films of MEH−PPI and MEH−PPV stored in dark and air or for those films stored under nitrogen atmosphere and exposed to light. It is clearly the combination of oxygen and light which is harmful for the polymer films.

In conclusion, a soluble conjugated aromatic poly(azomethine) with high molecular weight was obtained by substituting every second phenyl ring with a branched alkoxy side chain and a methoxy group. This polymer displayed very good photostability but exhibited poor photoluminescence efficiency, both in solution and in the solid state. Cyclic voltammetry showed oxidation and reduction processes with rapid loss of electroactivity after some cycles. The use of this polymer in photonic devices is presently under investigation.

Experimental Section. Polymer Synthesis. 1,4-Phenylenediamine (0.913 mmol, 98.6 mg) was dissolved in anhydrous toluene (15 mL) and lithium chloride (9.1 mmol, 380 mg) was added. The mixture was warmed to dissolve the diamine, and then the dialdehyde **1** (0.829 mmol, 242 mg) dissolved in anhydrous toluene (10 mL) was added to the solution at room temperature. The mixture was then refluxed under nitrogen atmosphere for 48 h. An excess of the diamine (0.45 mmol, 49 mg) was added and the mixture was refluxed for 1 additional hour. The polymer was isolated by precipitation into methanol (250 mL) and purified by Soxhlet extraction with methanol (24 h). The polymer was dissolved in chloroform (35 mL), filtered, and methanol (150 mL) was added dropwise. The polymer was isolated as an orange powder (262 mg, 87%).

Acknowledgment. This work was supported by the Swedish Research Council for Engineering Sciences (TFR). We thank Marie Björklund for the SEC measurements.

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MA9701090