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A study on the molecular weight of the chloro-precursor polymer to MEHPPV

Duncan W. J. McCallien, Andrew C. Thomas and Paul L. Burn*

The Dyson Perrins Laboratory, South Parks Road, Oxford, UK OX1 3QY

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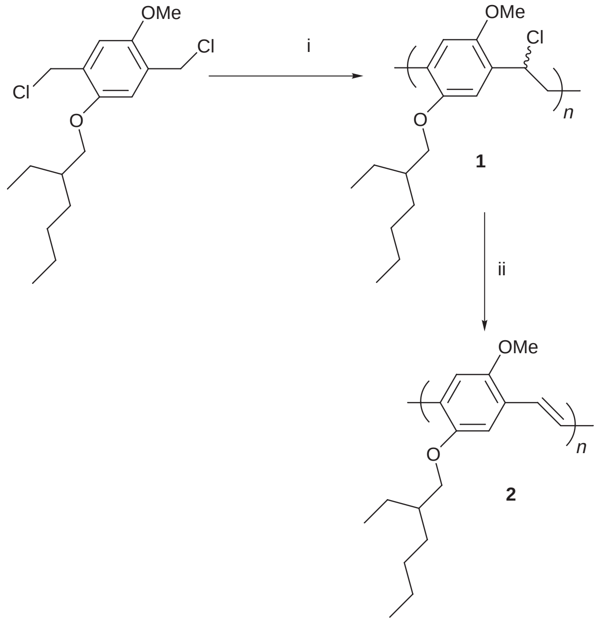
The observed molecular weight of the chloro-precursor polymer, 1, to poly[2-(2′-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEHPPV) was found to decrease with decreasing polymer concentration when measured by gel permeation chromatography with the decrease probably being due to the dissociation of polymer aggregates or physical networks.

One of the main driving forces for the continued interest in conjugated polymers was the discovery that they can be used as the light-emitting component in light-emitting diodes.[1] Conjugated polymers are designed so that they are either soluble in their conjugated form or are produced in an insoluble form *via* a precursor polymer.[2] The former route has the advantage that the syntheses are generally easier and processing straightforward whilst the latter route has the advantage that multilayer LEDs can be easily produced as the polymer can be rendered insoluble in the last step. For polymer based LEDs to work well a number of factors are required including balanced charge injection, good charge mobility through the material, and efficient emission from the singlet exciton. For each of these factors the interactions at the molecular level such as the formation of aggregates can play an important role.[3–6] Most of the studies on the aggregation of electroactive polymers have been carried out on the conjugated form[3–7] although there has been a study following aggregation which occurred during the conversion of a precursor polymer to poly(*p*-phenylene).[8] However, it is reasonable to expect that in the case of conjugated polymers prepared *via* precursor polymers the level and type of aggregation or film morphology observed in the final polymer could be affected by the aggregation or physical networks present at the precursor polymer stage. The precursor route to poly(1,4-phenylenevinylene) (PPV) and its derivatives has been widely studied with a number of derivatives being successfully produced *via* halo precursor polymers.[9–12] During our study of a chloro precursor route to an insoluble form of MEHPPV we discovered that the molecular weight of the chloro-precursor polymer when measured by gel permeation chromatography was not the same at different dilutions.[9] This observation has not been reported for other precursor polymers to PPV or its derivatives. In this communication we describe our initial results on the effect of polymer concentration on the observed molecular weight of the chloro-precursor polymer to MEHPPV.

The chloro-precursor polymer **1** was prepared by our recently reported method (Scheme 1).[9] The molecular weight dependence on concentration was first discovered when the chloro-precursor **1** was being analysed by gel permeation chromatography (GPC) (against polystyrene standards). We found on diluting concentrated samples of **1** to form dilute homogenous solutions suitable for GPC analysis that if the samples were analysed immediately they had a high $\bar{M}_w$, $>2\times10^6$. The $\bar{M}_w$ would 'decay' over several hours towards an equilibrium low $\bar{M}_w$ material (Fig. 1). A similar decay was also observed for $\bar{M}_n$. In addition, we found that the molecular weight was strongly concentration dependent even on small dilutions (Fig. 1). We equilibrated samples at full (≈ 15 mg ml^{-1}), half and quarter concentrations at room temperature overnight before diluting them 1 in 10 for GPC analysis. The initial $\bar{M}_w$ of the samples was seen to decrease from greater than 2×10^6 for the full concentration to 3.9×10^5 and 2.7×10^5 for the half and quarter concentrations respectively. The $\bar{M}_w$s of the half and quarter concentrations then further decayed on dilution.



Scheme 1 Synthesis of MEHPPV **2**. *Reagents and conditions*: i) K^+ $^-OBu^t$, THF; ii) heat.

The most striking effect of the difference in molecular weights was observed when the low molecular weight material was concentrated to the same mass/volume as the high molecular weight material and the two samples were spin-coated from solution. The reconcentrated, less viscous, 'low' molecular

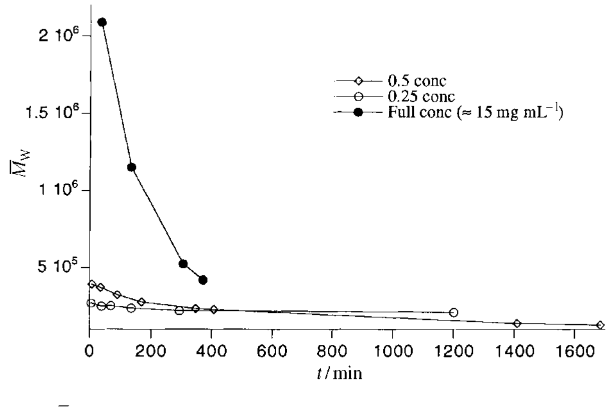


Fig. 1 $\bar{M}_w$ *vs.* time of equilibrated full, 0.5, and 0.25 concentrations on dilution.

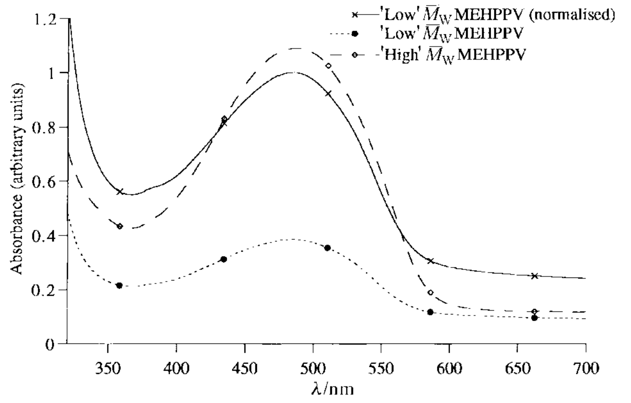


Fig. 2 Comparison of UV–visible spectra of MEHPPV prepared from 'low' and 'high' $\bar{M}_w$ **1**. We have also normalised the spectra of 'low' $\bar{M}_w$ to show the similar onset of absorption to the 'high' $\bar{M}_w$ MEHPPV.

weight material gave far thinner films than the 'high' molecular weight material. When the 'low' molecular weight sample of Cl-MEHPPV was spin-coated at 2000 rpm for one minute and converted at 220 °C for six hours it gave a coarse film of MEHPPV ($\sim$800 Å thickness; $\lambda_{max}=484$ nm, optical density $\approx$0.35). In contrast the 'high' molecular weight **1** when processed and converted under the same conditions gave a thicker film (1550 ± 50 Å; $\lambda_{max}=484$ nm, optical density $\approx$1.1) (Fig. 2).

Three potential reasons for the decrease in molecular weight observed by GPC are polymer degradation, change in polymer solution morphology, or the decomposition of physical polymer networks or aggregates. We have determined that the decrease in $\bar{M}_w$ is not due to the polymer chemically degrading to form low molecular weight polymers and oligomers. This was done by analysis of the samples by GPC, ^{1}H NMR, and infrared and UV–visible spectroscopy. It would be expected that if chemical degradation of the polymers were occurring then as the molecular weight decreased there would be oligomeric material formed. On following the molecular weight decrease the GPC traces showed no low molecular weight oligomers were being formed over the timescale of the experiment even when the molecular weight had changed by 95%. For the ^{1}H NMR studies samples of 'high' and 'low' molecular weight material were prepared so that the mass/volume of **1** in solution was the same in each. The ^{1}H NMR spectra of the 'high' and 'low' molecular mass solutions of **1** were identical and there was no difference in the broadness despite the differences in viscosities of the two solutions. Finally samples of the 'high' and 'low' molecular weight **1** were thermally converted to MEHPPV. The infrared spectra (Fig. 3) of the MEHPPV formed from the 'high' and 'low' molecular weight **1** were identical giving further evidence that chemical degradation was not occurring. In addition, the onset of absorption in the UV–visible spectrum of the two samples was similar suggesting that the effective conjugation length of the two materials was the same (Fig. 2).

The polymer solutions generally contained some propan-2-ol arising from the purification procedure.[9] Propan-2-ol is a poor solvent and so its presence in solution in varying amounts could affect the morphology or aggregation of **1** in solution and hence cause the variable molecular weights observed. This was discounted by allowing a solution of **1** (concentration $\approx$1.3 mg mL^{-1}) to equilibrate to a low molecular mass. The dilute solution containing 'low' molecular weight material was then concentrated to $\sim$26 mg mL^{-1} and precipitated with propan-2-ol. On collecting the precipitate and resolvating the material to 1.3 mg mL^{-1} the $\bar{M}_w$ had not increased and was 277 000 when run immediately (before reprecipitation it was 290 000). Similarly samples of 'high' or 'low' $\bar{M}_w$ material on evaporation to dryness and resolvation with tetrahydrofuran, thus changing the amount of any propan-2-ol present, did not show any change in molecular mass. We therefore conclude that the small amounts of remaining propan-2-ol do not have a major effect on the molecular weight of **1**.

As both chemical degradation and the effect of residual solvent do not appear to cause the observed decrease in $\bar{M}_w$ we believe that the observed phenomenon is due to the breaking down of polymer aggregates or physical networks which form during the polymerisation. Evidence for this was strengthened by carrying out the polymerisation at an initial monomer concentration of 0.04 M instead of the usual 0.4 M. By lowering the concentration of monomer in the polymerisation we found, as expected, that lower molecular weight **1** was formed, and that the effect of dilution on $\bar{M}_w$ was markedly smaller (Fig. 4). This shows that there was less aggregation or entangling with 'low' molecular weight **1** during its formation. In addition, when thin films of this 'low' molecular weight **1** were spin-coated (at the same mass/volume as the high $\bar{M}_w$ **1**) and converted, only thin films of MEHPPV (950 ± 50 Å) were formed. This is similar to the situation observed on concentrating equilibrated 'low' molecular weight polymer.

We therefore conclude that the observed variation in molecular weight is strongly concentration dependent and is probably due to the formation of aggregates or physical networks which arise during the synthesis. The true molecular mass of a sample of **1** must therefore be taken as its final steady value after equilibration at room temperature. We are currently investigating this phenomenon by small-angle neutron scattering and are also studying the effect of polymer concentration on molecular weight of different precursor routes to MEHPPV and other conjugated polymers.

Gel permeation chromatography separations were carried out with a Polymer Laboratories PLgel 5 micron Mixed C analytical column with a 5 micron guard column, and calibrated with polystyrene narrow standards in de-aerated tetrahydrofuran (analytical grade subject to 2 min sonication) with toluene as the flow marker. The $\bar{M}_w$ points near 2×10^6 in

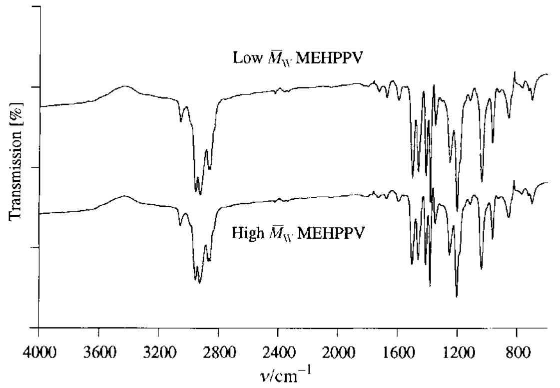


Fig. 3 Comparison of infrared spectra of MEHPPV prepared from 'low' and 'high' $\bar{M}_w$ **1**.

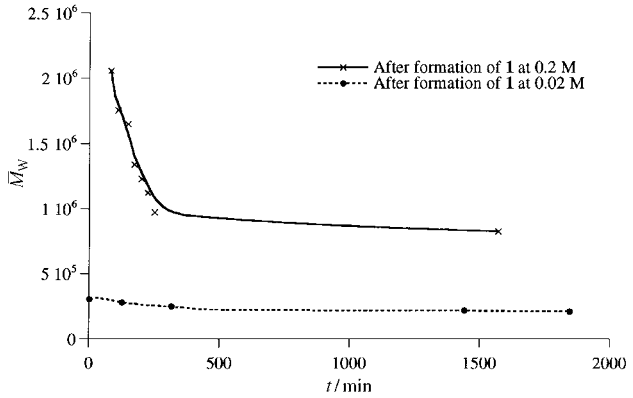


Fig. 4 Comparison of $\bar{M}_w$ *vs.* time for **1** prepared from 0.02 M and 0.2 M polymerisations.

Fig. 1 and 4 are above the calibration limit of the Mixed C column and are therefore probably overestimates of the actual $\bar{M}_w$. Nevertheless, the decrease in $\bar{M}_w$ is clearly observed. The flow rate was 1 mL min^{-1} and the flow was monitored by UV absorbance at 257 nm with the column at 22±1 °C. Spin-coated samples were prepared by covering a substrate with a solution of the precursor polymer and spinning this at 2000 revolutions per min for 60 s on a Dynapert PRS 14E spinner for photoresists, the solvent being allowed to evaporate under ambient conditions. Infrared spectra were recorded using KBr disks with a Perkin-Elmer Paragon 1000 infrared spectrometer. UV–visible spectra were recorded on a Perkin-Elmer Lambda 14P UV–visible spectrometer. Film thicknesses were measured with a Dektak^3 Surface Profilometer.

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