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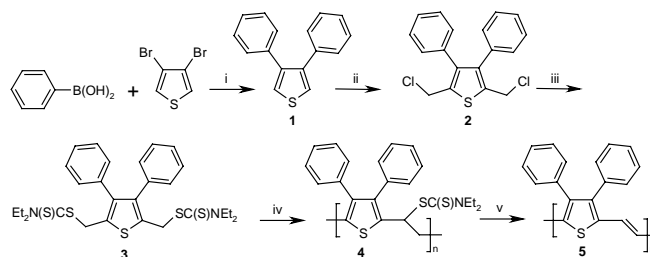
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# Low Band Gap Polymers via a New and Versatile Route: The Dithiocarbamate Precursor Route

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**Scheme 1.** Synthetic route towards the dithiocarbamate monomer **3** and polymer **5**. i: Pd(PPh<sub>3</sub>)<sub>4</sub>, KF, toluene/H<sub>2</sub>O; ii: CH<sub>2</sub>O, HCl, Ac<sub>2</sub>O; iii: NaSC(S)NEt<sub>2</sub>·3H<sub>2</sub>O, MeOH; iv: LHMDS, THF; v: ΔT.

## INTRODUCTION

In the last decade there is a great interest in low band gap conjugated polymers ( $E_g < 2.0$  eV) for their use as the active layer in polymer photovoltaic cells.<sup>1-5</sup> Polymer photovoltaics offer a significant technological potential as a renewable, alternative source for electrical energy. The demand for inexpensive renewable energy sources is the driving force for new approaches in the production of low cost polymer photovoltaic devices. One of the limiting parameters in these plastic solar cells is the mismatch of their absorption to the terrestrial solar spectrum. The solar emission has a maximum photon flux around 1.8 eV. The use of low band gap polymers expands the spectral region of bulk-heterojunction solar cells. As a result, these polymers offer a viable route to enhance the number of photons absorbed, which ultimately can give rise to better efficiencies. However, one of the problems in the synthesis of novel conjugated polymers in general is their insolubility. To overcome this problem, frequently precursor routes are employed. First a soluble non conjugated (precursor) polymer is prepared which subsequently can be converted into the conjugated form by a simple elimination.

Four major precursor routes are known: the Gilch precursor route,<sup>6</sup> the Wessling-Zimmerman precursor route,<sup>7</sup> the xanthate precursor route<sup>8</sup> and the sulfinyl precursor route.<sup>9</sup> These four routes usually perform well in the synthesis of poly(*p*-phenylene vinylene) (PPV) derivatives but all give unsatisfactory results in the synthesis of well defined low band gap polymers like poly(thienylene vinylene) (PTV). For that reason we developed a new precursor route in our laboratory: the dithiocarbamate precursor route.<sup>10</sup> As an example, we will report on the synthesis of poly(3,4-diphenyl-2,5-thienylene vinylene) (DP-PTV). The first attempt to synthesize this polymer via the dithiocarbamate precursor route only yielded moderate molecular weights<sup>11</sup>. Furthermore, the best temperature of reaction was  $-78^\circ\text{C}$  and the yields were rather low. Here we present an adaptation of this route. By changing the reaction conditions we have been able to increase the molecular weight and the yield dramatically. In addition, the reaction can now be carried out at room temperature.

## EXPERIMENTAL

**Monomer Synthesis.** The monomers are synthesized according to an earlier reported procedure.<sup>11</sup> Suzuki coupling between 3,4-dibromothiophene and phenylboronic acid yields the 3,4-diphenylthiophene **1** which is converted to the 3,4-diphenyl-2,5-bis(chloromethyl)thiophene **2** via chloromethylation. Subsequently, **2** is immediately converted into the monomer, 3,4-Diphenylthiophene-2,5-diyldibismethylene *N,N*-diethyl dithiocarbamate **3**, via reaction with sodium diethyldithiocarbamate trihydrate. (Scheme 1) The overall yield from the starting compound toward **3** is 54 %.

**Polymerization.** Polymerization of **3** to the precursor polymer **4** has been carried out using different reaction conditions (cf. entries 1-4, Table 1). The same polymerization procedure as reported earlier<sup>11</sup> has been followed except lithium hexamethyldisilazide (LHMDS) has been used as base instead of LDA.

**Thermal conversion of 4 into 5 in a thin film.** Thin films of precursor polymer **4** can be converted into the conjugated polymer **5** by a simple thermal treatment.

## RESULTS AND DISCUSSION

**Synthesis.** In Table 1 the polymerization results are summarized. For comparison, also the results obtained with LDA<sup>11</sup> as the base, instead of LHMDS, are included. The weight-average molecular weights ( $M_w$ ) of **4** have been determined by analytical SEC in DMF using polystyrene standards. The observed molecular weight distributions for **4** are monomodal with  $M_w$  values ranging from  $82.9 \times 10^3$  to  $708.3 \times 10^3$  for polymerization with LHMDS and from  $24.6 \times 10^3$  to  $50.4 \times 10^3$  for those polymerized with LDA. (cf. entries 1-4, Table 1). It is clear from these values that polymerization with LHMDS as the base gives rise to polymers with much higher molecular weights. LHMDS is less basic, more stable and much less sensitive to air as compared to LDA. As a result, even at  $25^\circ\text{C}$  polymerization occurred where polymerization at ambient temperatures with LDA did not yield polymer due to the strength and instability of LDA.

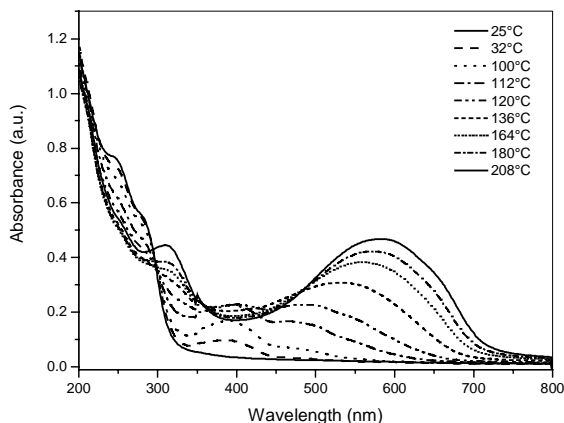
Both the higher polymerization temperature and the higher molecular weights are significant advantages from an industrial application point of view. High  $M_w$  polymers have better film forming properties which is crucial for device preparation. Furthermore, recent papers<sup>12,13</sup> correlate the charge carrier mobility in devices to the molecular weight of the polymer. It has been shown that high molecular weight polymers exhibit better mobility. In view of these reports, in the near future the mobility of our polymers will be determined as well.

**Table 1. Comparison of the Polymerization Results with LHMDS and LDA**

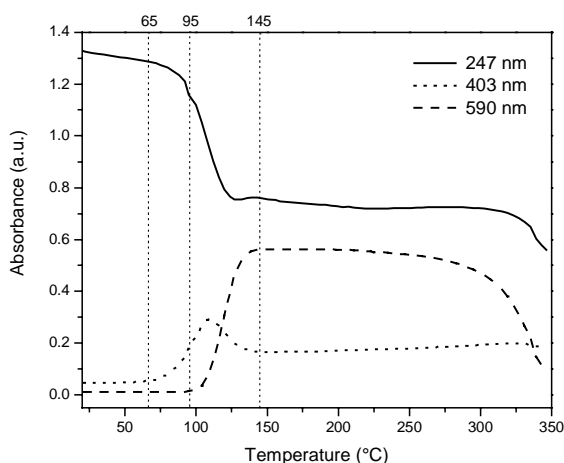
Entry	Polymerization Temperature	LHMDS			LDA		
		$\eta$ (%)	$M_w$ ( $\times 10^3$ )	PD	$\eta$ (%)	$M_w$ ( $\times 10^3$ )	PD
1	$-78^\circ\text{C}$	60	708.3	3.3	40	29.4	1.2
2	$-78^\circ\text{C} \rightarrow 0^\circ\text{C}$	55	625.7	3.1	35	24.6	1.2
3	$0^\circ\text{C}$	68	82.9	3.4	20	50.4	1.4
4	$25^\circ\text{C}$	56	89.8	3.5	0	/	/

**Optical properties.** The formation of **5** in a thin film is well visible in the temperature dependent UV-Vis absorption spectrum by the development of a band with  $\lambda_{\text{max}} = 550\text{-}600$  nm and the decrease of the absorption of **4** at  $\lambda_{\text{max}} = 247$  nm (Figure 1). When looking at the absorbance profiles (Figure 2) one can clearly see an increase in absorbance at 590 nm between  $110^\circ\text{C}$  and  $160^\circ\text{C}$ , i.e. the formation of the conjugated system. It is also visible from Figure 2 that the thermal stability of the conjugated system is  $300^\circ\text{C}$ .

The room temperature absorption maximum  $\lambda_{\text{max}}$  of a thin film of **5** is 600 nm. The band gap of **5** can be derived from its absorption characteristics by drawing the tangent on the low energetic edge of the absorption spectrum, which corresponds to a band gap of 1.70 eV. The optical properties of these polymers are identical to those synthesized with LDA.<sup>11</sup> This is normal since the  $M_w$  does not have an influence on the absorption characteristics of conjugated polymers, which are determined by the effective conjugation length of typically 8-10 monomeric units.



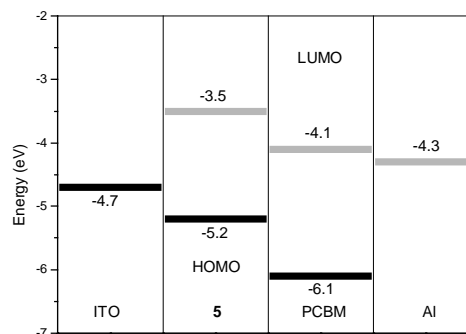
**Figure 1.** Temperature dependent UV-Vis spectra of the conversion of **4** into **5**.



**Figure 2.** UV-Vis absorbance profiles at 247, 403 and 590 nm as function of temperature during the conversion of **4**.

**Electrochemical properties.** Cyclic voltammetry (CV) was employed for the estimation of the relative position of HOMO/LUMO levels of **5**. The HOMO and LUMO levels are determined from the onset of oxidation and reduction, respectively. In the anodic scan, the onset of oxidation of **5** occurs at 0.35 V vs. Ag/Ag<sup>+</sup>, which corresponds to a HOMO energy level of -5.2 eV. The onset of reduction is at -1.38 V vs. Ag/Ag<sup>+</sup> and a LUMO energy level of -3.5 eV. The electrochemical HOMO/LUMO gap of 1.73 eV is in good agreement with the band gap derived from UV-Vis spectroscopy.

Figure 3 displays the resulting energy band diagram in relation to the relative energy levels of the most widely used acceptor in organic solar cells, PCBM and the work function of indium tin oxide (ITO) and aluminum (Al), which are usually employed as electrodes in polymer solar cells. The HOMO of polymer **5** is distinctively higher in energy than that of PCBM. However, not the HOMO energy levels but the relative positions of the donor LUMO and the acceptor LUMO are important for the intended charge transfer. The difference between the LUMO of **5** and PCBM is around 0.6 eV which is sufficiently high to allow for an unrestricted and directed charge transfer. These results, together with the results of the UV-Vis spectroscopy (band gap of 1.70 eV and  $\lambda_{\text{max}}$  of 600 nm), confirm that conjugated polymer **5** is an excellent candidate for the active layer in organic solar cells. Hence, further research will be done to incorporate this polymer in solar cells.



**Figure 3.** Energy band diagram with HOMO/LUMO levels of **5** and PCBM in relation to the work function of ITO and Al.

## CONCLUSION

In conclusion, the synthesis of **5** via the dithiocarbamate precursor route has been optimized by changing the base from LDA to LHMDS. This results in high molecular weights, even at a polymerization temperature of 25°C. It has been shown that **5** has a low band gap (1.7 eV) as derived from absorption spectroscopy and electrochemistry. Together with its suitable HOMO/LUMO energy levels (-5.2 eV and -3.5 eV, respectively), this material is an excellent candidate for application in organic solar cells.

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