

Fractionated regioregular poly(3-hexylthiophene). Spectroscopic and electrochemical studies

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RÉSUMÉ

Le poly(3-hexylthiophene) régiorégulier a été synthétisé et fractionné en quatre fractions de masses moléculaires (M_n) différentes présentant de faibles indices de polymolécularité. Les spectres UV-VIS confirment l'augmentation de la longueur de conjugaison moyenne avec l'accroissement de M_n . Les voltammogrammes des fractions confirment les résultats UV-VIS et montrent que la contribution des segments faiblement conjugués diminue avec l'augmentation de M_n .

Mots-clés : poly(3-alkylthiophenes), polymère régiorégulier, fractionnement

ABSTRACT

Regioregular poly(3-hexylthiophene) was obtained and fractionated into four fractions of different molecular weights (M_n) exhibiting low polydispersity coefficients. UV-VIS spectra confirm the increase of average conjugation length with the increase of the M_n of fractions. Voltammetric curves of fractions corroborate UV-VIS results and show that the contribution of poorly conjugated segments decrease with the M_n .

Keywords : poly(3-alkylthiophenes), regioregular polymer, fractionation

INTRODUCTION

Both electronic and optical properties of poly(3-alkylthiophenes) (P3ATs) are very sensitive towards the structural homogeneity of the polymer. It is, therefore, very important to synthesize the polymer with the least possible number of defects of its structure. Initially applied methods of P3AT synthesis were not regiospecific [1]

till recently two groups [2,3] independently developed preparation methods leading to regioregular polymer. However taking into account a rather low molecular weight of thus obtained polymers their properties may depend on macromolecular parameters. For this reason a fractionation of regioregular poly(3-hexylthiophene) (R-P3HT) has been undertaken. In the next step spectroscopic and electrochemical properties of R-P3HT as a function of the M_n have been studied.

EXPERIMENTAL

R-P3HT was synthesized using a modification of the method of McCullough et al. [4]. After precipitation with CH_3OH the crude polymer was extracted consecutively with acetone, hexane, CH_2Cl_2 and THF. Each time the fraction soluble in each solvent was separated. Four fractions differing significantly in M_n with small polydispersity coefficients were obtained (Table I). It is interesting to note that the value of D_p approximately doubles for each consecutive fraction. The purity was checked by ^1H NMR. The degree of regioregularity exceeded 96% for each fraction [5], thus the conjugation length should be also limited by the chains termination (M_n of the polymer). This conclusion is manifested in the UV-VIS spectra (Fig. 1). Bathochromic shift of the λ_{max} for consecutive fraction proves evidently an increase of the average conjugation length with increasing M_n . The fine

Table I : Macromolecular parameters of fractions

M_n - number average molecular weight,
 P_i - polydispersity coefficient,
 D_n - degree of polymerization

	fraction	wt%	M_n	P_i	D_n
1	acetone	6.5	2280	1.38	14
2	hexane	9.7	4380	1.22	26
3	CH_2Cl_2	33.1	8370	1.33	50
4	THF	49.2	17700	1.45	106

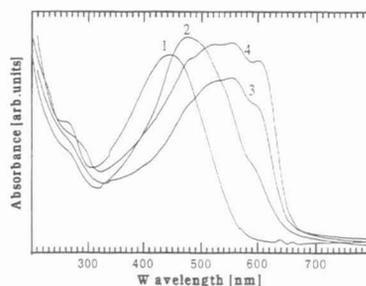


Figure 1 : UV-VIS spectra of fractions (films cast from THF solution)

vibrational structure is more pronounced for longer fractions which is consistent with enhanced conjugation, better planarity and higher crystallinity of these fractions [6]. The spacing between the 1st and the 2nd shoulders corresponds to vibrational transitions involving C=C stretching observed in Raman spectra of R-P3ATs [7].

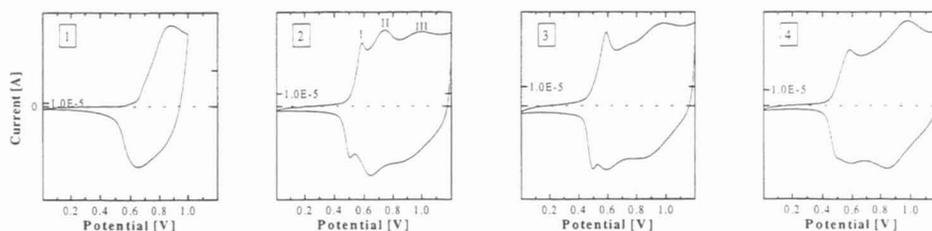


Figure 2 : Cyclic voltammograms of thin films deposited on Pt electrode (Pt foil as a counter electrode, vs Ag/AgCl, 0.1 M Bu₄NBF₄/acetonitrile solution, 20mV/s)

The cyclic voltammetry results (Fig. 2) corroborate the UV-VIS data. The first (I) and the third (III) redox peak correspond to the two step (polaron-bipolaron) oxidative doping of defect-free chain segments of R-P3ATs with relatively long conjugation [8]. The relative intensity of these peaks increase with the increase of the M_n . On the contrary, the intensity of second (II) peak, which can be attributed to the doping of less conjugated segments, successively decrease. Thus it can be concluded that the contribution of poorly conjugated segments decrease with the M_n of polymer.

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