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## Synthesis, characterization and molecular weight studies of certain soluble poly(3-alkylthiophene) conducting polymers

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**Abstract** Soluble conducting polymers of 3-hexylthiophene, 3-octylthiophene, 3-decylthiophene and 3-dodecylthiophene were synthesized by constant potential electrolysis. The resultant polymers were characterized by cyclic voltammetry, ultraviolet spectroscopy, thermogravimetric analysis and differential scanning calorimetry. Molecular weights were studied with gel permeation chromatography on solutions of the polymers in toluene. Surface properties were investigated by scanning electron microscopy. Substituent groups' lengths have been found to strongly influence the electronic properties of the resultant polymers. Poly(3-hexylthiophene) has shown the highest conductivity, with the highest degree of polymerization. The conductivity and the degree of polymerization values decrease as the substituent chain length increases.

**Keywords** 3-Alkylthiophenes · Gel permeation chromatography · Molecular weight · Soluble conducting polymers

### Introduction

Conducting polymers, especially polypyrroles and polythiophenes, have attracted great attention in recent years because of their potential applications [1]. Despite their short history, they have found a place in various application areas such as rechargeable batteries,

non-linear optics, gas separation membranes, gas sensor, enzyme immobilization, etc. [2, 3, 4, 5]. However, owing to their insolubility, infusibility and poor mechanical properties, they had limited processability and utility. In order to improve these poor properties, either they were synthesized as blends and graft copolymers [6, 7] or they were synthesized chemically and doped subsequently [8]. These afterwards-doped conducting polymers have been reported to be processable, but they do not exhibit as high conductivities as electrochemically synthesized and self-doped polymers. Thus they are not suitable replacements for electrochemically synthesized ones.

With the synthesis of the first soluble poly(3-alkylthiophene)s, researchers have focused on this new family of conducting polymers. The electrical properties and solubilities of these polymers have been studied extensively [9, 10, 11]. However, a comprehensive comparison and explanation of molecular weight effects on the electronic properties has not been reported.

In this study, the solubilities and molecular weights of poly(3-alkylthiophene)s with four different side chains, namely poly(3-hexylthiophene) (P3HT), poly(3-octylthiophene) (P3OT), poly(3-decylthiophene) (P3DT) and poly(3-dodecylthiophene) (P3DoT), have been investigated. We have examined the relation between the molecular weight and the length of the side chain. Along with the molecular weight studies, thermal, spectroscopic and surface properties are also reported.

### Experimental

The electrochemical polymerization of all four 3-alkylthiophenes was carried out under a constant potential of 1.8 V, in a three-electrode, one-compartment cell. Round platinum plates of 1.5 cm diameter were used as working and counter electrodes. The electrodes were immersed in 6 M nitric acid solution before use. Tetra-butylammonium tetrafluoroborate solution (0.1 M) in acetonitrile was used as the electrolyte. The monomer concentration in each experiment was 0.01 M. Argon

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gas was bubbled throughout all the experiments. The polymers were peeled off from the electrode surface as very thin films for subsequent study. All potentials were reported versus the Ag/AgCl reference electrode.

## Results and discussion

### Cyclic voltammetry

Cyclic voltammograms of all four monomers were studied between 0.5 V and 2.0 V, with a scan rate of 20 mV/s. A gradual positive shift in the oxidation potential of the monomers is observed with increasing side-chain length. The peak oxidation potential increased from 1.75 V for 3-hexylthiophene (3HT) to 1.85 for 3-dodecylthiophene (3DoT), with the values for 3-octylthiophene (3OT) and 3-decylthiophene (3DT) lying in between, around 1.80 V.

### Differential scanning calorimetry

DSC thermograms of the poly(3-alkylthiophene)s do not exhibit particular transitions. However, a glass transition kind of behavior is observed for P3HT, P3OT and P3DT around 220, 215 and 212 °C, respectively. The same kind of transition was not observed for P3DoT. Substitution of an alkyl chain and increasing the chain's length increases the flexibility of the polymer.

### Thermogravimetric analysis

All of the polymers were subjected to heating from room temperature to 400 °C at a rate of 10 °C/min. The TGA thermogram of P3HT, compared to the thermograms of the other three polymers, lost less of its original weight, over the same temperature range, with 56% of P3HT still in the heating pan after 400 °C. The remaining weight percentages for P3OT, P3DT and P3DoT were 51%, 48% and 40%, respectively.

### Conductivities and molecular weights

Table 1 gives a summary of the conductivities and the molecular weights of the resultant polymers. The conductivities of polythiophene and poly(3-methylthi-

ophene) (P3MT), obtained from literature [12, 13], are also given for comparison.

Molecular weight values tend to decrease with increasing side-chain length, but there is not a specific trend when molecular weights alone are compared. Comparison of average degrees of polymerization, however, reveals a definite trend. The decrease in the degree of polymerization with increasing side-chain length is correlated with the increase of the molecular weight of the starting monomer.

In order for the polymer to grow, it needs to be attached to the electrode surface, as the electron transfer takes place near or at the surface. Increasing the length of the side chain of the monomer makes the growing polymer so bulky and amorphous that it flakes off the electrode surface. Then new, more mobile monomers diffuse to the electrode, and the process repeats itself. Thus, at any given time, the molecular weight of the polymer that is attached to the electrode surface is not higher than a certain number of monomer units. This effect can be seen by the change of color in the P3DoT synthesis cell, being the heaviest monomer of all four.

Conductivity values also show a decreasing behavior with increasing side-chain length. The substitution of bulky alkyl side chains decreases the degree of coplanarity, and hence yields a lower conjugation of the rings in the polymer film.

Combining the conductivity and degree of polymerization, we can also speculate about the conduction mechanism in the polymers. With the increasing side-chain length, the degree of polymerization decreases from 28 for P3HT to 14 for P3DoT (2:1). However, the conductivity value drops from 18 S/cm to 0.8 S/cm (22.5:1) for the same two polymers, i.e. by more than one order of magnitude. Thus, the conduction is not directly related to the main chain length, but rather the distances between the main chains, which also is related to the ease of electron hopping. Increasing the side-chain length increases the distance between the main chains owing to the bulkiness of the side chains. This results in more space between chains, and makes it more difficult for electrons to move from one chain to another, resulting in lower conductivity. By taking the effect of the side chain on coplanarity into account, this clearly explains the overall decrease in the conductivity values upon increasing side-chain length.

The behavior in the DSC thermograms can be explained better with the molecular weight information.

**Table 1** Summary of molecular weights and conductivities

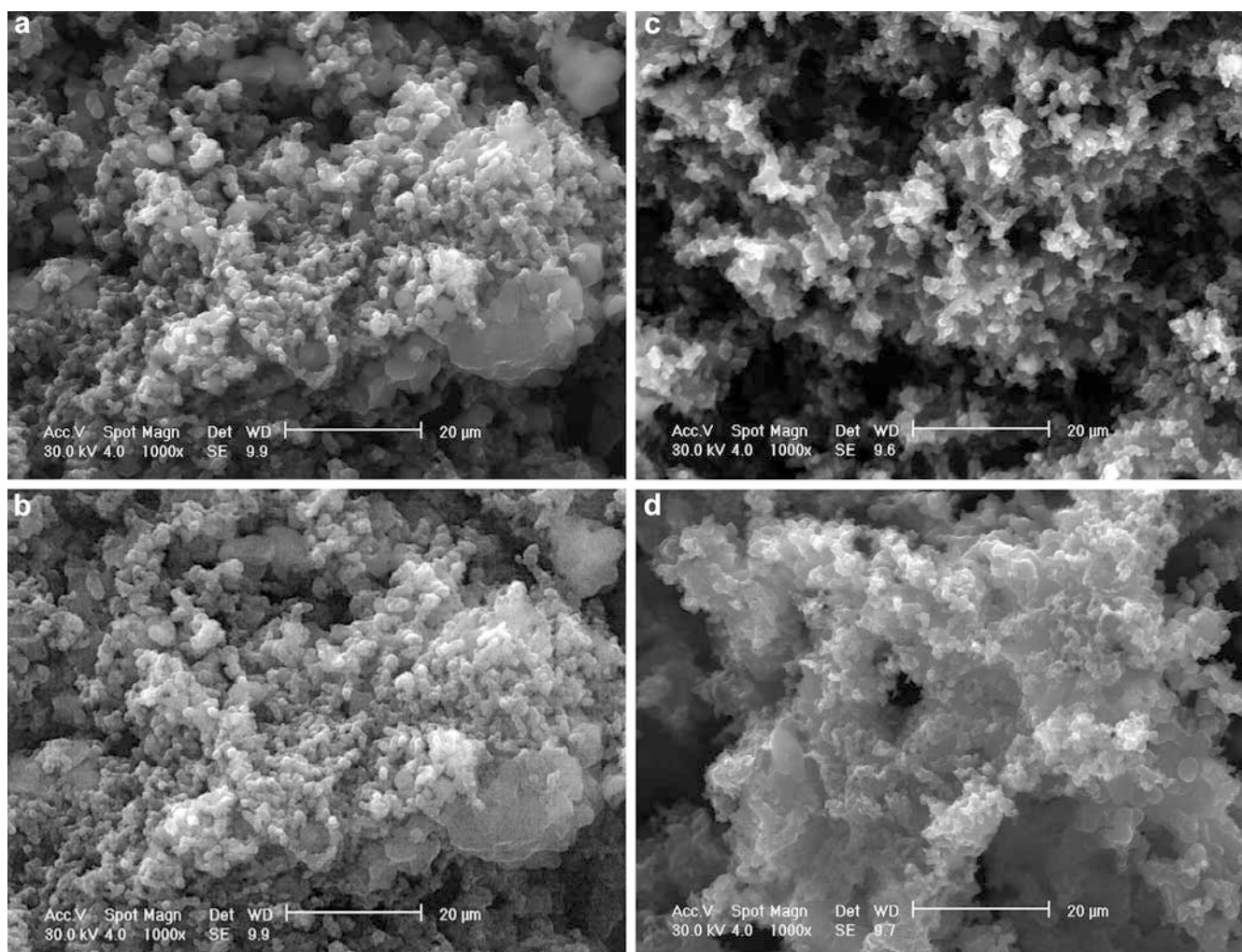
Monomer	Molecular weight (monomer) (g/mol)	Molecular weight (polymer) (g/mol)	Av. degree of polymerization	Conductivity (S/cm)
Thiophene	84.13	–	–	49
3-Methylthiophene	98.16	–	–	43
3-Hexylthiophene	168.30	4700	28	18
3-Octylthiophene	196.36	4200	22	15
3-Decylthiophene	224.41	4300	19	3
3-Dodecylthiophene	252.47	3500	14	0.8

The higher length of the main chain in P3HT increases the polarizability of the  $\pi$ -electron system, thus contributing more to the van der Waals interaction energy and increasing the thermal stability of the polymer.

### Scanning electron microscopy

The planarity of most heterocyclic conducting polymers (polypyrrole, polythiophene, etc.) is the main reason for the cauliflower-like structures that are obtained in electron micrographs [1]. The studied polymers, being neither very long nor three-dimensionally networked, did not exhibit the cauliflower-like structure (Fig. 1). P3HT (Fig. 1a), having the longest main chain of all four, showed some small globular structures but still no cauliflower structures. However, as the side chain becomes longer and coplanarity decreases, these globular structures also tend to disappear (Fig. 1b–d).

**Fig. 1** SEM micrographs of (a) poly(3-hexylthiophene) (P3HT), (b) poly(3-octylthiophene) (P3OT), (c) poly(3-decylthiophene) (P3DT) and (d) poly(3-dodecylthiophene) (P3DoT)



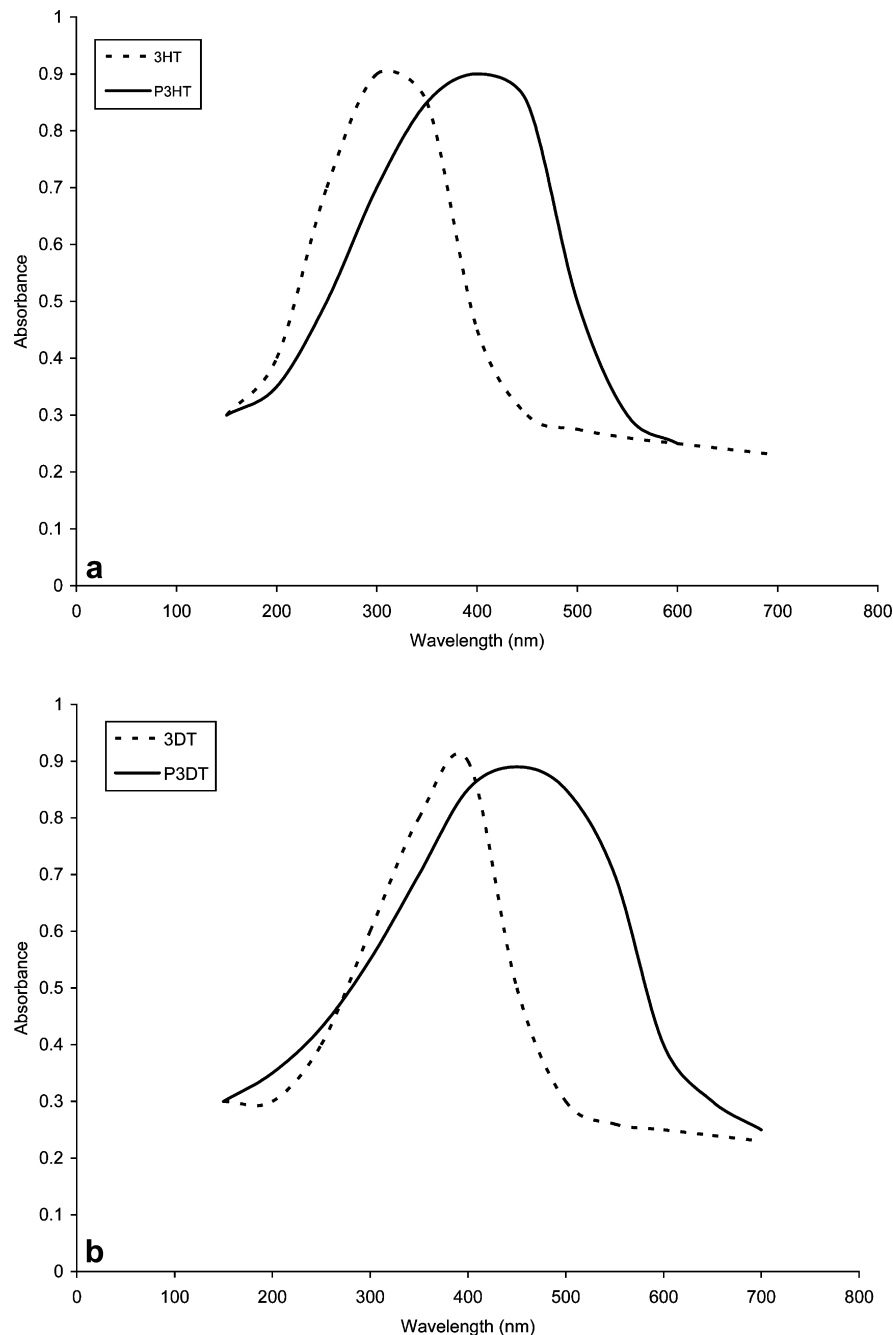
### Ultraviolet spectroscopy

Comparison of the UV spectra of the monomers and polymers (Fig. 2) shows the increase in conjugation on polymerization, by the shift of the curves towards higher wavelengths. The amount of each wavelength shift decreased with the increasing side-chain length. The shift that is observed for the 3MT and P3MT pair is more than 100 nm (305 nm to 410 nm), whereas that for the 3DT and P3DT pair is 60 nm (390 to 450 nm). The breadth of the polymers' spectra also increased as the side chain's length increased.

### Conclusion

Soluble conducting polymers of 3-hexylthiophene, 3-octylthiophene, 3-decylthiophene and 3-dodecylthiophene were synthesized electrochemically. Conductivities, molecular weights and degrees of polymerization of the polymers strongly depend on the side chain's length. The substitution of alkyl side chains decreases the reactivity of the growing chain, and with the increasing side-chain length, all three properties show a decrease.

**Fig. 2** UV-Vis spectra of (a) 3HT and P3HT and (b) 3DT and the P3DT



Conductivity is mainly due to hopping between the chains, rather than on a chain, for these polymers.

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