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Mobile Charge Carriers in Pulse-Irradiated Poly- and Oligothiophenes


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Abstract

Lower limits of the intrinsic charge carrier mobility in the solid phase of a series of oligothiophene compounds were determined with the pulse-radiolysis time-resolved microwave conductivity technique, PR-TRMC. The mobility values fall roughly into two regimes and show no correlation with the number of conjugated thiophene units. Relatively low mobilities (in the range of 3-6 \(10^{-6}\) cm\(^2\)V\(^{-1}\)s\(^{-1}\)) were found for a series of cyclohexyl-endcapped thiophenes, while significantly higher values of 0.01-0.02 cm\(^2\)V\(^{-1}\)s\(^{-1}\) were obtained for several n-hexyl and n-dodecyl substituted compounds and for sexithiophene. Interestingly, these latter values are similar to those of n-alkyl substituted polythiophenes measured earlier.

Keywords: Polythiophene and derivatives, conductivity

1. Introduction

Thiophene oligomers have been successfully incorporated in organic Thin Film Transistors (TFTs), acting as the semiconducting layer in these devices [1]. However, the reported charge carrier mobility values vary over a wide range for the various compounds studied by different groups. This stems from the fact that the results depend strongly on factors such as the macroscopic organisation of the polymer film, the presence of impurities and the quality of electrode contacts.

With the pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) technique [2] it is possible to obtain information on the intrinsic charge transport properties of polycrystalline materials. Charge carriers are produced in a powder sample by irradiation with high-energy electrons, and the resulting conductivity is monitored with microwaves of low field strength (ca. 10 V/cm). This high-frequency ac detection method has the advantage of probing the conductivity in small microdomains, implying that effects due to domain boundaries are minimised. Earlier, this technique was applied to a series of three n-alkyl substituted polythiophenes [3], yielding mobility values that were very similar to each other, irrespective of the side-chain length. In the present paper the polythiophenes are compared to a number of thiophene oligomers, varying in conjugation length and alkyl-substitution.

2. Experimental

The structures of the thiophene compounds studied are shown in Figure 1. Their preparation and structural characterization has been published elsewhere [4].

In the PR-TRMC experiment [2] bulk samples of 20-200 mg are irradiated with short pulses (2-20 ns) of 3 MeV electrons from a Van de Graaff accelerator, resulting in a uniform distribution of electron–hole pairs throughout the sample. The radiation-induced increase in conductivity (\(\Delta \sigma\)) is monitored as a change in the microwave power reflected by the cell containing the sample, yielding time-resolved information. A lower limit to the sum of positive and negative charge carrier mobilities \(\Sigma +U\) is derived from the dose-normalized end-of-pulse conductivity \(\Delta \sigma/D\) using an estimate of the energy needed to form an electron–hole pair, and assuming that all of these pairs survive to the end of the ionisation pulse. Correction for the geminate recombination process might yield \(\Sigma +U\) values that are a few times higher than \(\Sigma +U\).

![Fig. 1: Structures of the oligo- and polythiophenes studied.](image-url)
3. Results and Discussion

In Figure 2 the $\Sigma \mu_{\text{sum}}$ values of the various thiophene compounds at room temperature are plotted versus the inverse number of thiophene units. It is clear that two regimes can be distinguished: relatively high mobilities in the range of 0.01-0.02 cm²/Vs are found for the n-alkyl substituted compounds and for unsubstituted sexithiophene (6T), while low mobilities (3-6 $10^{-4}$ cm²/Vs) are obtained for the cyclohexyl end-capped series ECnT. In both cases there is no apparent effect of the number of conjugated thiophene units, which is best demonstrated by the fact that the polythiophenes studied earlier [3] do not show higher mobilities than their oligomeric counterparts. These results are in line with the finding in TFT experiments that the charge carrier mobility in conjugated thiophene compounds is highest in the direction perpendicular to the long axis of the molecules [1]. This would explain the remarkably similar mobility in the various oligo- and polymers, provided that the molecules are packed parallel to each other with a relatively short interchain distance, which allows for efficient chain-to-chain charge transport. The lower values of the end-capped series ECnT could then be explained by taking into account the non-planarity of the cyclohexyl groups, which prevents the thiophene chains from achieving an optimal configuration for interchain charge transport.

In Figure 3, the conductivity transient of di-n-dodecyl-substituted sexithiophene (DD6T) is compared to that of unsubstituted 6T, to illustrate the influence of alkyl substitution on the decay kinetics of the mobile charge carriers. It can be seen that although their end-of-pulse values are similar, DD6T has a much longer conductivity half-lifetime ($\tau_{1/2} = 70$ ns) than 6T ($\tau_{1/2} = 5$ ns). This effect might be attributed to the fact that the alkyl side-chains of DD6T act as insulators that prevent the rapid three-dimensional recombination of the charge carriers occurring in 6T.

Furthermore, in comparing samples of 6T (as well as 4T) from different sources it was found that $\tau_{1/2}$ becomes even shorter for less purified samples, leading to much lower end-of-pulse conductivity values. In case of 4T, no $\Sigma \mu_{\text{sum}}$ values above 0.001 cm²/Vs were obtained, but it is not clear whether this is an intrinsic property of the molecules or only due to impurities. Nevertheless, these aspects should also be considered when selecting appropriate materials for applied device studies.

"This implies that $\Sigma \mu_{\text{sum}}$ might be three times higher than $\Sigma \mu_{\text{intrinsic}}"