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SPECTRA OF OLIGOTHIOPHENES WITH LIMITED NUMBER OF 3-ALKYL-SUBSTITUENTS: INFLUENCE OF AGGREGATION.

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Abstract Absorption and emission spectra of the title oligothiophenes, both in chloroform solution and as solid (or in PMMA ss), are given. Evidence is found for the simultaneous existence of various conformers that differ markedly in their conjugation lengths.

INTRODUCTION

In previous papers [1,2] we reported on the preparation and various physical properties of a series of α,α'-coupled oligomers of thiophene containing 3,4,5,6,7,9, and 11 rings and provided with 0 to 5 side groups (*n*-butyl, *n*-dodecyl or *tert*-butyl). The synthesis leads, in general, to a mixture of isomers differing only in the position (3 or 4) of the *n*-alkyl groups in a certain ring. The oligomers are, as before, denoted by the shorthand notation illustrated below.

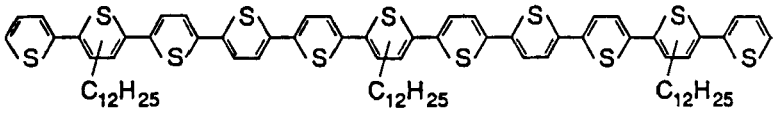

Fig. 1. Compound T_{11} d_3(2,6,10) *i.e.* 11 α, α'-coupled thiophene rings (T_{11}) bearing 3 dodecyl groups (d_3) at rings (2,6,10).

It was concluded that in these partially substituted oligomers of thiophene the conjugation length increases with the number of coupled thiophene rings, and decreases slightly with the number, the length, and a closer approach of the alkyl groups. At 11 thiophene rings saturation of conjugation length is approached, but not reached.

In this paper it will be shown that the visible absorption and emission spectra depend strongly on the state of aggregation. In general, the shape of the emission spectrum is independent of the wavelength of the excitation radiation, as long as it is well within the absorption band. However, for a special case, *viz. a dilute solid solution in a PMMA matrix, the shape of the emission spectrum* varies markedly with excitation wavelength. This is interpreted as being due to the presence of various conformers in the samples, which tend to agglomerate separately.

EXPERIMENTAL

The preparation and characterization of the various oligomers have been described previously [1,2]. Spectra were recorded with the aid of a Varian

Superscan3 UV-vis spectrometer and a Perkin Elmer LS-50 luminescence spectrometer, respectively.

Solid-state absorption spectra were measured on thin films on quartz glass, obtained by evaporating chloroform or chlorobenzene solutions or spin-coating chlorobenzene solutions of the oligomers. In the same way solid solutions in a PMMA matrix (0.2 to 2 wt%) were obtained. The solvents were used as received (Merck p.a.), the PMMA was Elvacite 2009 (Dupont).

ABSORPTION SPECTRA

The absorption spectra of the compounds in chloroform solution all show a single broad band, whose maximum shifts towards longer wavelengths with increasing length of the molecules. In general the medians of the absorption of solid films are at higher wavelengths than those of the solutions in chloroform, which points to a higher conjugation length in the solid (more bending around the interring bonds in the solutions because of entropy effects). Characteristic examples are given in Fig. 2.

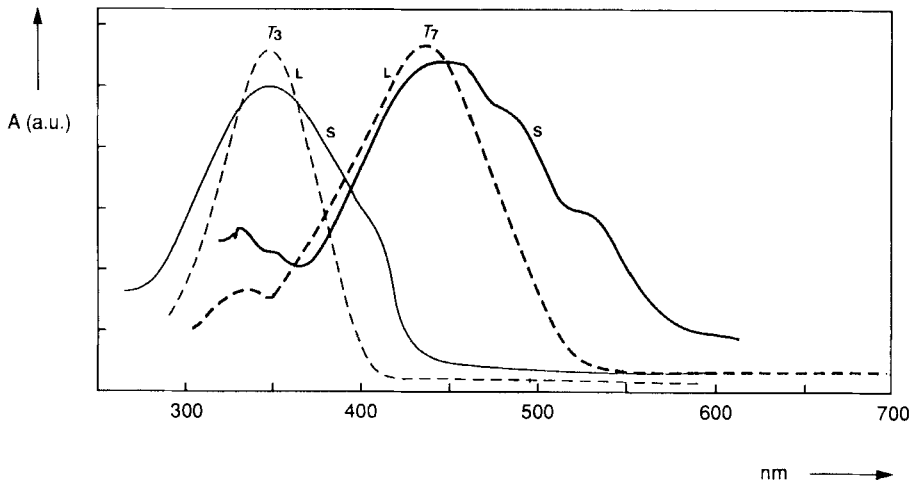

Fig. 2. Absorption spectra of T_3 $d(2)$ and of T_7 $d(4)$ in chloroform solutions (dotted lines) and as solid films (solid lines).

The lower oligomers show side peaks or shoulders at higher wavelengths, just as found in unsubstituted oligothiophenes [3]. In the absorption spectra of solid films of the higher oligomers, especially those bearing dodecyl side chains, a clear distinction between main peak and side bands becomes impossible (see Fig. 4).

The spectra of the oligomers in diluted solid solutions (a few wt %) in PMMA are very similar to those of the pure solids. However, at very high dilution the spectra in PMMA become similar to the chloroform solution habitat, albeit that for T_9 and T_{11} the peak values are at a slightly lower wavelength (about 10 nm)

in the PMMA solid solutions. On the other hand, concentrated solutions in chlorobenzene tend to develop side peaks too. It is, therefore, probable that the multimaxima spectra are caused by aggregates or small crystals.

In general (*e.g.* [3,4]) the presence of structure in the absorption spectra of such solids is ascribed to phonons (vibrational side bands). Because of the very high intensity and large number of maxima, we questionned this interpretation for the spectra of the higher oligomers of thiophene [1]. A mixture of various conformers that differ in conjugation length either by the number of transoid and cisoid ring connections or by rotations around the interring bonds may be a better proposal.

EMISSION SPECTRA

The emission spectra of the oligothiophenes in chloroform solution consist of two bands and a shoulder (see Fig. 3), independent of the wavelength of excitation as long as it is well within the absorption band (tested to A > 0.25 A max). The shape of the spectra is very similar to that of poly(3-hexylthiophene) [5], indicating that the emitting excitations (neutral bipolarons?) in the oligomers and polymer are similar too.

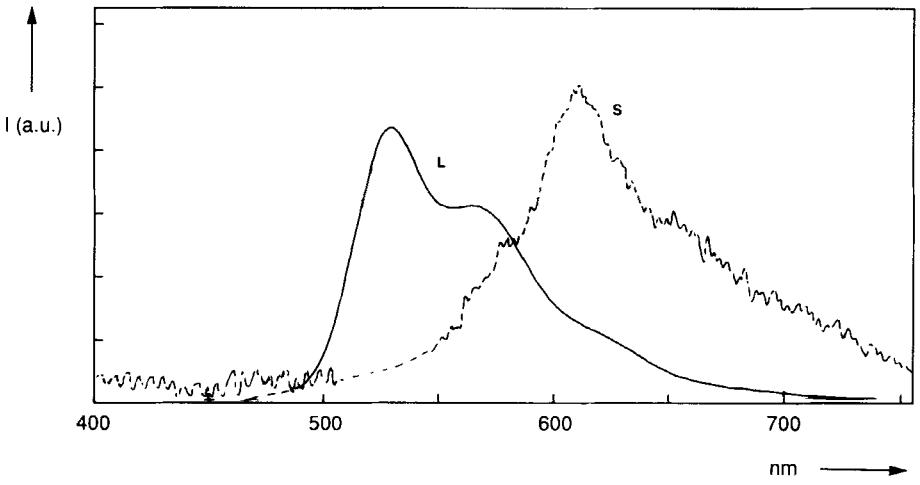

Fig. 3. Emission spectra of T_7 *d*(4) in chloroform solution (L) and as solid film (S). The shape of the spectra is independent of the excitation wavelength.

The emission spectra of the solid films have a similar shape to those from the oligomer solutions in chloroform, but are shifted up to 0.3 eV to lower energies. This again points to a longer conjugation length in the solid state. In many cases the low energy shoulder is missing or less clear. Films of solid solutions in PMMA give emission spectra that are, in general, identical with those of the solid films.

However, in some diluted solid solutions we found that the emission spectra did change markedly by varying the excitation wavelength. The result on the sample in which this effect was most clear is given in Fig. 4. It is seen that the emission spectrum shifts to lower energy with higher excitation wavelengths and suggests that each 'peak' in the absorption spectrum corresponds with a peak in the emission spectrum.

The absorption spectrum of Fig. 4 is practically invariant for alternate preparation conditions. In fact, it is nearly identical with that of a thin solid film of the oligomer. Only if the solvent is evaporated at high temperatures (100 °C) are the 'peaks' at 520 nm and 560 nm relatively reduced. The emission spectra, however, depend strongly on the exact preparation conditions. In pure solid films as well as in many dilute solid solutions in PMMA only a single spectrum similar to (a) is observed, independent of the excitation wavelength. Only in samples prepared from homogeneous, dust-free dilute solutions with fairly slow evaporation of the solvent at low temperatures (20-35 °C), is a dependence on the excitation wavelength observed, although this is in most cases still restricted to a change of a (a) type spectrum to a (b) type.

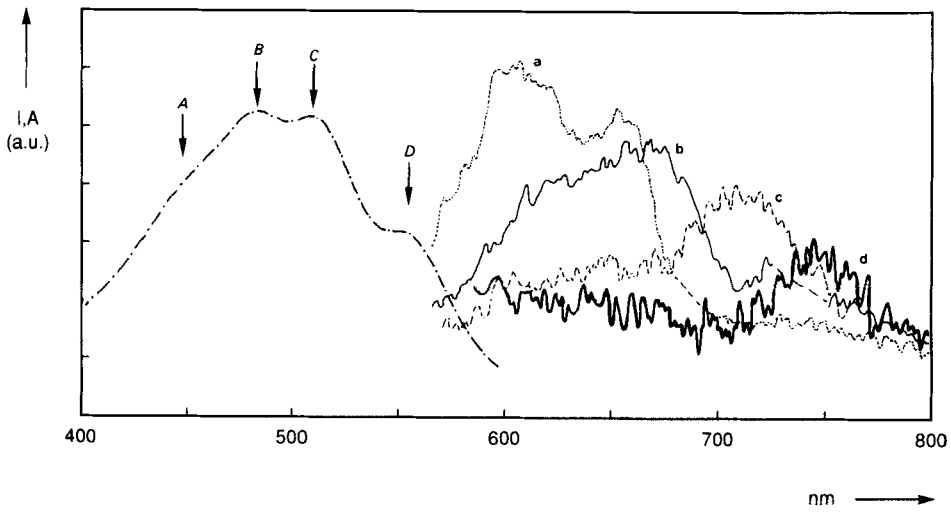

Fig. 4. Absorption spectrum of T_{11} d_3(2,6,10) as solid solution (2 wt %) in PMMA films and its emission spectra (a,b,c,d) excited at wave lengths (A,B,C,D), respectively.

If the structure of the absorption spectrum were due to vibrational side bands, the dependence of the emission spectrum on the exciting wavelength is hard to explain. However, if the absorption spectrum is merely the sum of the spectra of conformers having different conjugation lengths, an explanation follows quite naturally. During the evaporation of the solvent the solution becomes oversaturated and in the first instance aggregation of like conformers

will occur. In bulk and in most solid solutions the aggregates of the various conformers are not spatially separated, but are in close contact with each other. Moreover, if one allows a rapid solidification of the oligomer, one may expect that even a single aggregate will contain a mixture of different conformers. Transfer of excitation energy is easy, and all excitations end at the favourate emission sites. In carefully prepared solid solutions, however, we expect that the clusters of like conformers will remain separated from each other by the PMMA matrix. Transfer of the excitation energy from one cluster to another will be hampered and emission will occur at the most favourate site within each cluster. In fact, this model leads to conformers that absorb and emit radiation fairly independently. This is exactly what is shown in Fig. 4.

If the solid is formed at higher temperatures, the abundance of conformers with the highest conjugation length (possibly all stretched molecules) will decrease because of its lower entropy content. This explains the observed decrease of the 'peaks' at 520 nm and 560 nm in the absorption spectrum of such samples.

CONCLUSIONS

In partially substituted oligomers of thiophene the conjugation length measured by the UV-vis absorption spectra is smaller in solutions than in solid state. In the solid state of the longer oligomers various conformers with different conjugation length are present simultaneously. This is evidenced by the shape of the absorption bands, but more strongly by the dependence of the emission spectra of certain samples on the excitation wave length.

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