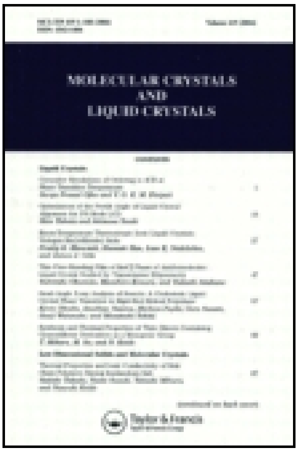

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TOWARDS THE EFFECTS OF CONJUGATION LENGTH ON PHOTOINDUCED SPECIES.

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Abstract Optical absorption and photoinduced absorption measurements of a series of endcapped oligo-enes are reported: clear trends are seen as a function of chain length.

INTRODUCTION

It is well established that the properties of polymers are strongly dependent on the details of their structure: this has been explained in terms of the degree of disorder present within materials and, in particular, in terms of effective conjugation length[1]. In seeking a deeper understanding of polymer properties, much of the effort has been directed at the synthesis of very long chain polymers, however, there is always a distribution of chain lengths within such materials.

As an alternative approach we have studied a series of endfunctionalised oligo-enes of intermediate chain length and low polydispersity, which were synthesised via a living polymerisation process, based on the Durham route to polyacetylene[2]. Preliminary optical absorption and photoinduced absorption spectra of these materials are reported here and show clear trends in properties. It is hoped eventually to study truly monodisperse samples of short chain analogues, solubilised by judicious choise of endgroups.

EXPERIMENTAL DETAIL

The five endcapped oligo-enes (with m nominally equal to 13, 21, 45, 101 or 181) were synthesised via the reaction scheme shown in Figure 1. Absorption spectra were recorded at room temperature using a Perkin Elmer λ19 Spectrophotometer, both in solution and in the solid state. Photoinduced absorption spectra were recorded at 8K using a helium refrigerated cryostat, Chromex monochromator, silicon photodiode and indium arsenide detectors: the 458 nm output of an argon ion laser was used to provide photoexcitation. For solution state measurements the converted polymers were dissolved as far as possible in either acetonitrile or pentane and contained in quartz cuvettes. For solid state measurements, thin films of the polymers were prepared by spin-coating the precursors onto sapphire substrates prior to thermal conversion.

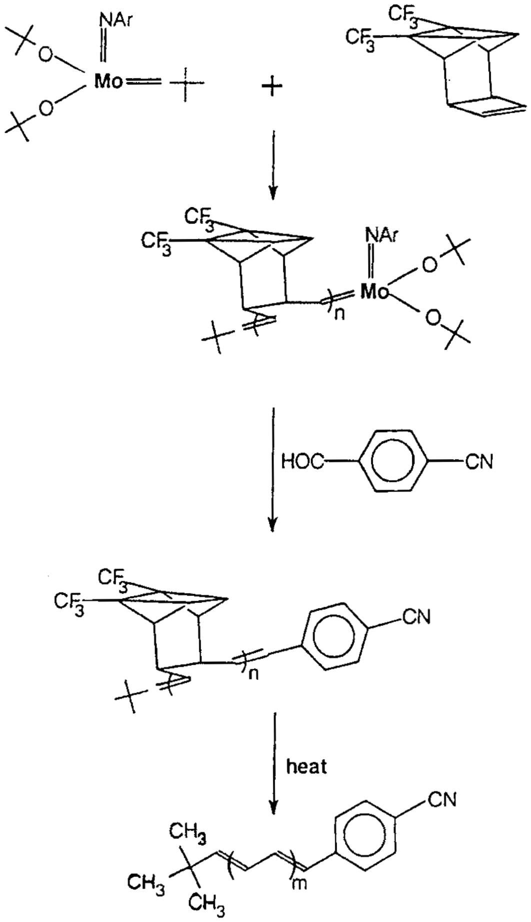
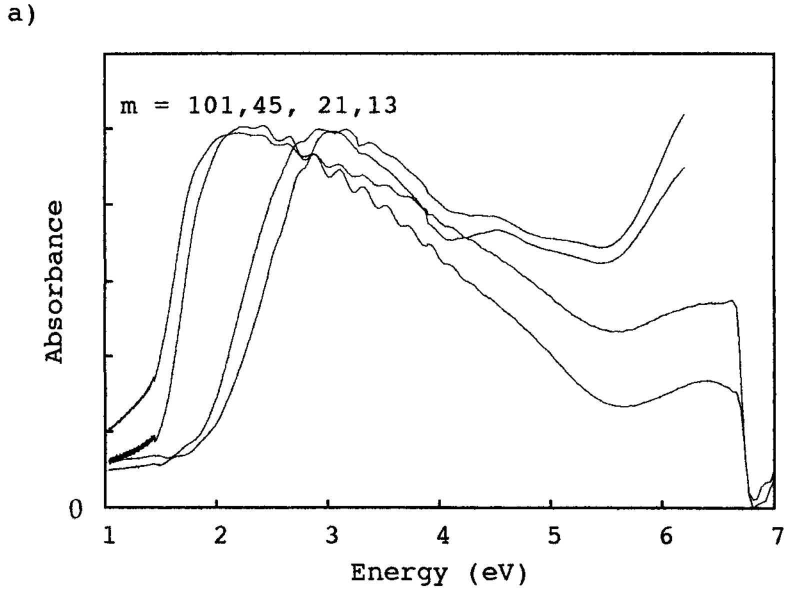


FIGURE 1 Reaction scheme for the synthesis of 4-cyano phenyl capped terbutyl oligo-enes of length m.



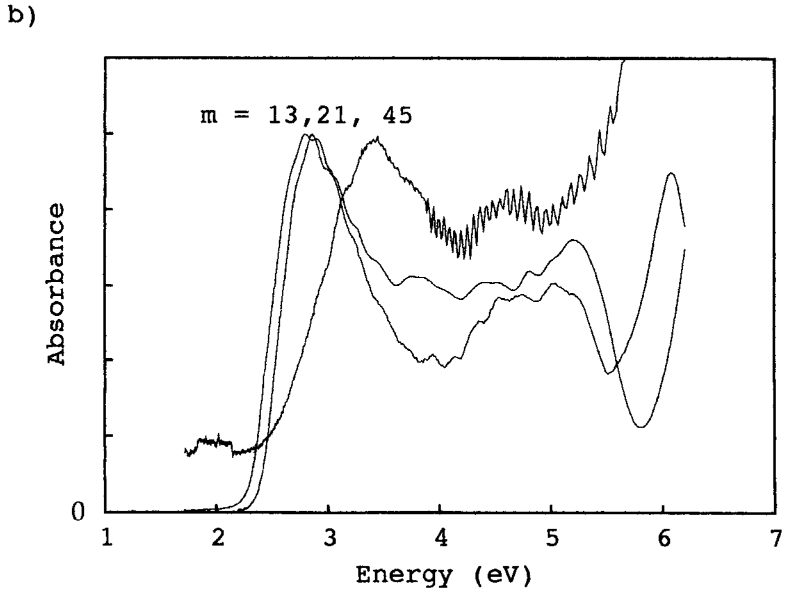


FIGURE 2 Optical absorption spectra of the endcapped oligo-enes in a) solid state and b) solution (labels show order of peaks).

RESULTS AND DISCUSSION

The results of the room temperature absorption measurements are shown in Figure 2. The spectra are normalised to the same peak size to bring out the shift in the peak position: in fact, the peak absorption decreased with m in solution, due to the lower solubility of the longer polyenes, whereas in the solid state the optical density of the films was determined by sample thickness.

In the solid state spectra, the peaks shift to lower energy with increasing chain length as expected, becoming more or less indistinguishable from *trans*-polyacetylene by the time a length of about 45 double bonds is reached. In the solution state spectra, however, the peaks unexpectedly shift in the opposite direction. Whilst it is clear that apart from the shortest oligomers, solubility is very low and it is likely that only the short chain fraction of the material is dissolving, this would lead to a more or less constant absorption energy. Two possible explanations are that as the chain length of the soluble portion of the samples increases so does the propensity for cis-trans isomerism or alternatively, greater delocalisation of the π-electrons on the longer chains could give a large change in the interaction with the solvent and a length dependent solvatochromism. We intend to explore this effect further.

The solution and solid state spectra of the two shortest oligomers show clear vibronic structure - a series of approximately regularly spaced secondary peaks superimposed on the main absorption peak - consistent with a small distribution of effective conjugation lengths within these samples. Although not such a good solvent as acetonitrile, pentane was also used in the hope that the secondary structure would become clearer, which it unfortunately did not. Note that the apparent secondary structures in the spectra corresponding to m = 45 and 101 are artefacts.

The photoinduced absorption spectrum of the longest chain sample (Figure 3a) compares very well with that of *trans*-

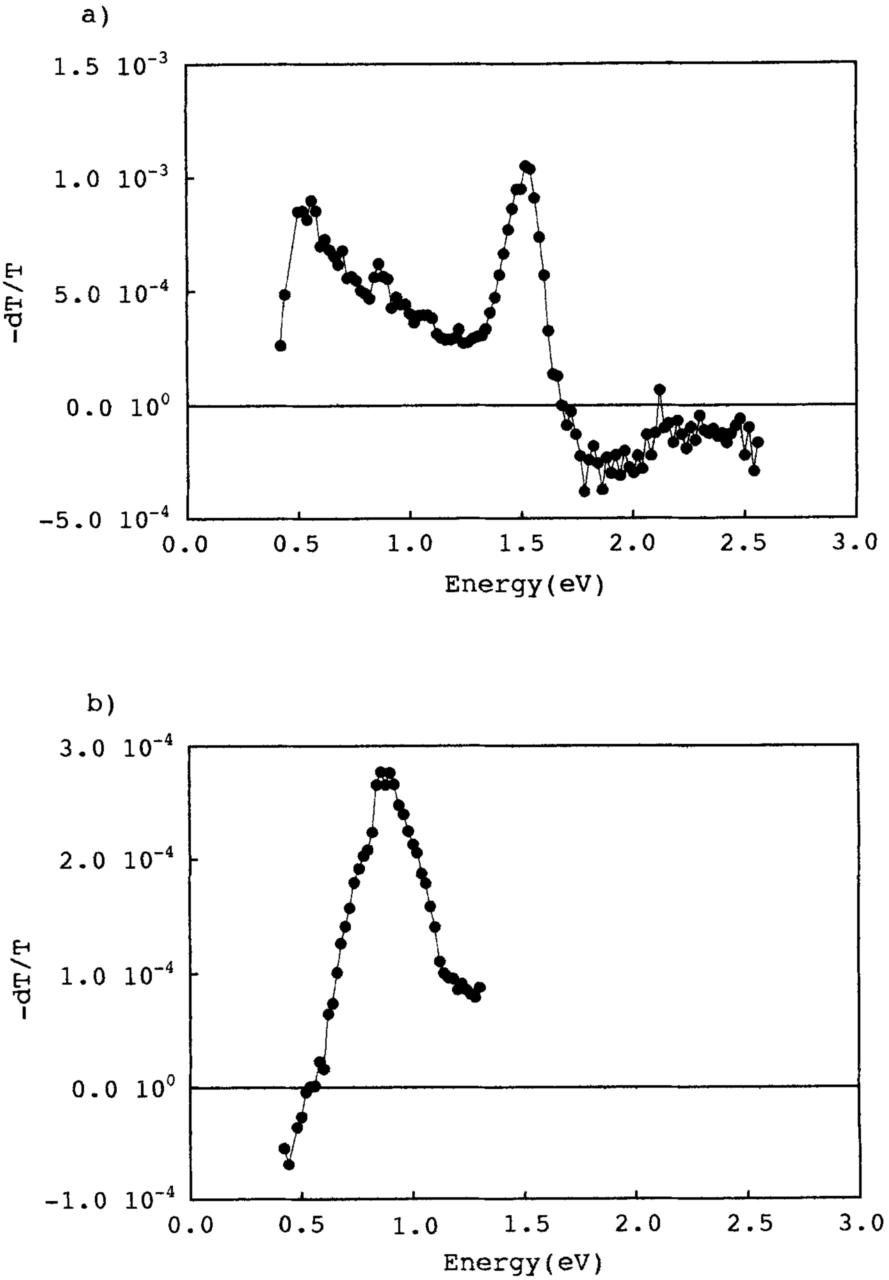


FIGURE 3 Photoinduced absorption spectra of a) m = 181 and b) m = 45 endcapped oligo-enes measured at 8 K.

polyacetylene. There are peaks at about 0.55 eV and 1.55 eV with bleaching peaking at 1.8 eV (compare 0.43 eV, 1.32 eV and 1.7 eV)[3], although there is no sign of the electromodulation feature at the band edge[4]. The 45 double bond oligomer (Figure 3b) has a broad peak - of similar width to the 0.55 eV peak above - centred at about 0.9 eV. If this is associated with charged solitons, as we might expect, then it indicates that photoexcited species are far more strongly affected by chain length than is the Peierls gap. Further experiments are underway in order to track the energies of photoexcited species with chain length.

Summary

These preliminary results show the expected chain length dependence of optical absorption spectra, but indicate that the behaviour of photoexcited species is less straightforward.

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REFERENCES

1. P. R. Surján and H. Kuzmany, Phys. Rev. B, 33, 2615 (1986).
2. K. Knoll and R. R. Schrock, J. Am. Chem. Soc., 111, 7989 (1989).
3. N. F. Colaneri, R. H. Friend, H. E. Schaffer and A. J. Heeger, Phys. Rev. B, 38, 3960 (1988).
4. J. Orenstein, G. L. Baker and Z. Vardeny, J. Phys. Colloq., 44, C3-407 (1983).