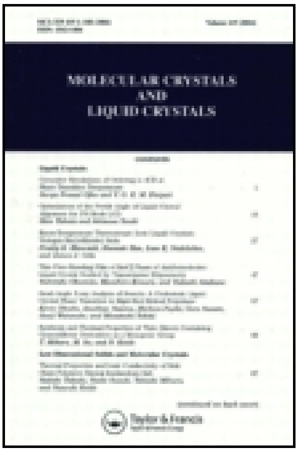

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Photoexcitations in Conjugated Copolymers

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PHOTOEXCITATIONS IN CONJUGATED COPOLYMERS

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Abstract We report in this short paper a preliminary account on the optical characterization and photoexcitation of a class of novel conjugated polymers consisting of regularly alternating thiophene and benzene sequences, which might represent models for one-dimensional superlattices. Optical absorption and emission spectra suggest that the barriers produced by the phenylene moieties do not interrupt the conjugation but can produce localization effects. Resonant Raman spectra indicate that a selective response of the thiophene and phenylene moieties occurs by varying the excitation energy from visible to ultraviolet. Moreover these measurements confirm the presence of a confinement on the thiophene blocks, while the biphenyl moiety does not appear to feel the energy barrier and behaves as a poly(paraphenylene) oligomer of 5-6 ring length. CW photomodulation spectra show that the formation of long-lived bipolarons takes place only if the thienylenic moiety is long enough to accomodate the lattice distortion.

INTRODUCTION

It is well known that conjugated polymers or conjugated long chain molecules are good candidates for application in optoelectronics and photonics as they exhibit fast and relatively large non linear optical response.[1] As a matter of fact, due to their quasi one-dimensional electronic structure, conjugated polymers can be regarded as natural quantum wires for which an efficient electronic polarization is produced when an external electric field is applied along the direction of the chain.

The motivation of the present work stems from the prediction[2] that a strong enhancement of $\chi^{(3)}$, up to 10^{-6} esu, can be expected upon sharpening the absorption bandwidth. The reduction of the dimensionality from "1" (conjugated polymer or quantum wire) to "0" (conjugated block copolymer or quantum dot) changes the sawtooth behaviour of the density of states into a singular behaviour[3] which can be broadened by inhomogeneous distribution of energies or by finite lifetimes effects. With this in mind we have designed and prepared a series of *regularly* alternating copolymers whose translational unit consists of a sequence of thiophene rings of various length (T_2,T_3 and T_6) connected to a sequence of benzene rings (B_1 and B_2) by an azomethine link.[4]

The regular alternation of low-energy gap (thienylenic moiety) and high-energy gap therefore yields a structure that can be considered, in principle, a model for a one dimensional superlattice. An attempt to synthesize polymeric superlattices has been done by Jenekhe[5] by alternating oligothienylenic segments and their quinoid counterparts. These polymers exhibit large third-order optical non linearities measured by time-resolved degenerate four-wave mixing.[6]

RESULTS AND DISCUSSION

Absorption spectra were recorded with a Cary 2400 spectrometer at room temperature. Raman spectra were obtained in the NIR with a Bruker Fourier trasformer spectrometer (IFS66+FRA106) exciting with the 1064 nm line of a Nd-YAG laser and in the visible with a Jasco TRS300 polychromator exciting with the lines of an Ar^+ laser. Photoinduced absorption spectra were obtained using a mechanically chopped cw Ar^+ laser as the pump and a tungsten halogen lamp as the probe. Monochromated optical transmission is measured with a cooled PbS detector and a photomultiplier tube and recorded by a phase-sensitive lock-in amplifier. Measurements have been performed on KBr pellets under vacuum at room temperature and at 80K.

Electronic and Raman spectra

Figures 1 and 2 show the absorption and emission spectra of T_3B_2 and T_6B_2 polymers. The position of the absorption edge, red shifted with respect to the absorption of the parent oligomers T_3 and T_6, is indicative of the fact that the barriers existing between the thienylenic and the phenylenic moieties do not break the conjugation and therefore the copolymer can be regarded as made of quantum dots rather than of π non interacting residues. The relatively large width of the absorption is probably due to inhomogeneous broadening, caused by disorder introduced by the polymerization reaction. We are presently looking for better controlled polymerization conditions, since we feel that a reduction of the disorder could result in the appearance of sharper features in the absorption spectrum characteristic of the quantum dot structure.[3]

The emission spectra of the copolymers do not vary for visible or uv excitations up to 4.4 eV. This is indicative of the fact that,regardless the type of the absorbing moiety, the radiative recombination takes place on the thienylenic segment in agreement with the fact that it corresponds to the potential well.

An extensive vibrational analysis of these block copolymers is reported elsewhere.[7] Here, we focus our attention on the Raman bands from which some information on the

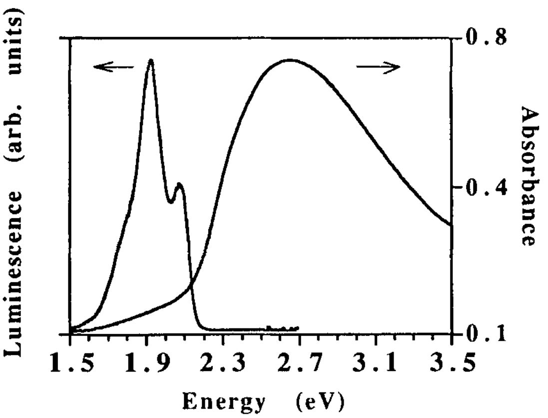

FIGURE 1 Optical absorption at 300 K and photo-luminescence at 77 K of T_3B_2.

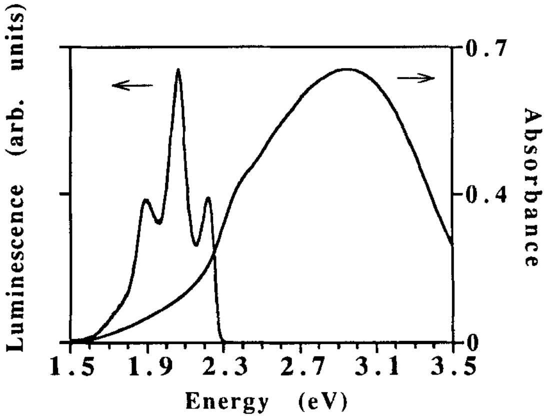

FIGURE 2 Optical absorption at 300 K and photo-luminescence at 77 K of T_6B_2.

confinement on the blocks of the copolymers can be obtained. For sake of brevity, we will discuss the T_3B_2 polymer only. In Figure 3 the Raman spectra of the pristine T_3B_2 are reported at two exciting wavelengths. The intensity dependence of the Raman bands upon the exciting frequency suggests that only the vibrations localized on the thiophene rings are resonantly enhanced by visible excitation. By exciting at 363 nm an enhancement of the phenylenic ring vibration is observed.

The degree of conjugation of the block copolymer can be inferred from the analysis of specific peak positions. In fact, an extensive study on the spectra of the thiophene oligomers[7,8] indicates that the Raman band around 1530 cm^{-1} undergoes a systematic down-shift as the number of conjugated thiophene rings increases. Moreover, for the phenylene moiety a band at 410 cm^{-1}, present in the polyparaphenylene (PPP) polymer, disappears in the B_2 oligomer.[7] On the basis of these considerations, the presence of a Raman band at 1530 cm^{-1} and another at 412 cm^{-1} in the T_3B_2 polymer can be interpreted by considering that the thienylenic segment feels the presence of the domain walls while

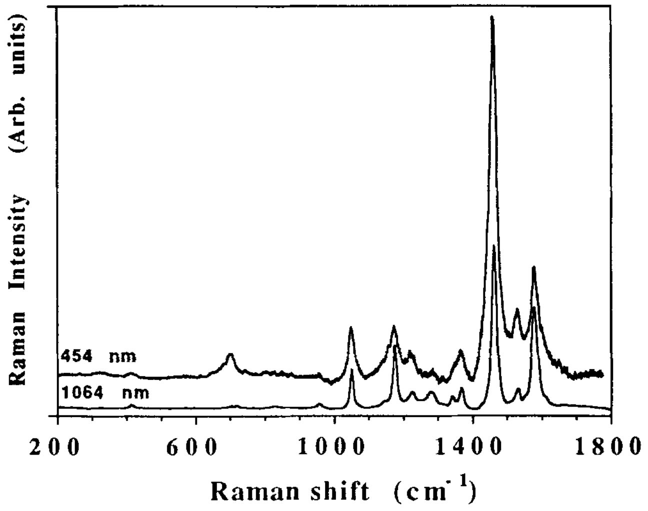

FIGURE 3 Raman spectra of T_3B_2 in the resonance (454.5 nm) and preresonance (1064 nm) conditions.

the biphenyle does not see any conjugation barrier and behaves as the homopolymer PPP. By analysing the intensity ratio of two phenylenic vibratrions an effective conjugation length of 5-6 rings can be inferred[7] for the phenylenic blocks.

CW photomodulation spectroscopy

This spectroscopical technique[9] measures the changes undergone by the absorption coefficient $\Delta\alpha$ upon photoexcitation. Namely the difference between the absorption of a sample containing a non equilibrium carrier concentration and the absorption of the ground state. This technique, which is sensitive to non equilibrium excitations in *all* states, gives complementary information to that obtained from cw photoluminescence which is limited *only* to radiative processes. Moreover this technique is limited only to excitations possessing relatively long lifetimes, namely 10^{-3}-10^{0} sec.

In Figure 4 is reported the photomodulation spectrum of T_6B_2 at 77 K obtained by exciting at 488 nm. Three peaks at 0.7 eV, 1.25 eV, 1.95 eV, plus a fourth peak at 2.3 eV, probably due to electroabsorption, are observed. The dependence of the peaks on temperature, chopper frequency and laser fluence clearly indicates that the peaks at 0.7 and 1.25 eV have the same origin. In particular these two peaks exibit square root dependence on the laser intensity while the peak at 1.95 eV is almost linear.

The analysis of these spectra indicates that bipolaronic states on the thienylene moieties are formed in T_6B_2. This is supported by the observation of the two electronic bands at

0.7 eV and 1.25 eV, which, in the case of the T_6 molecular crystal, are observed at 0.74 eV and 1.47 eV[10] and, in the case of polythiophene (PT), are at 0.45 eV and 1.25 eV.[11] These shifts are consistent with the lower gap of polythiophene. The origin of the electronic peak at 1.95 eV is less clear, its linear dependence on the laser power could be indicative of a triplet exciton polaron but its temperature independence contrasts this assignment. Another possibility is to relate this peak, which is absent both in the photoinduced spectrum of T_6 and PT, to the formation of interface states trapped between the two blocks of the copolymer.

In Figure 5 is shown the photoinduced spectrum of T_3B_2. One strong peak at 1.7 eV is observed together with a weak shoulder at 1.1 eV. A bleaching centered at 2.1 eV and a possibly thermal modulation at 2.4 eV are also observed.

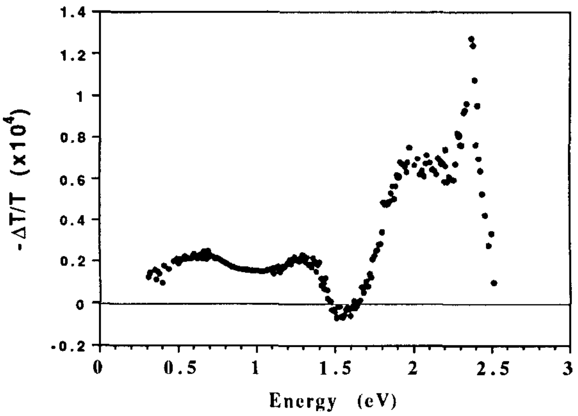

FIGURE 4 Photoinduced absorption of T6B2 excited at 488 nm at 77K.

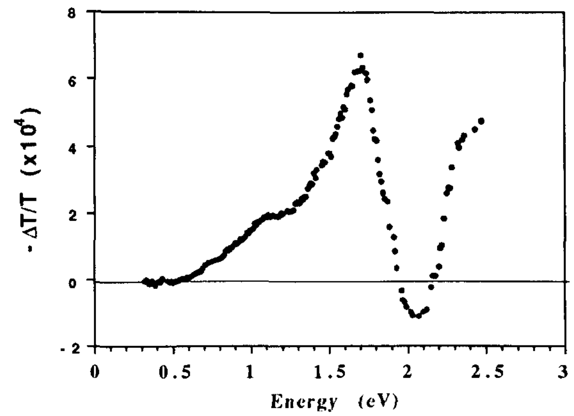

FIGURE 5 Photoinduced absorption of T_3B_2 excited at 488 nm at 77K.

The position, the shape and the intensity of the two photoinduced bands, which depend sublinearly on the laser intensity, indicate that they are not related to self trapped states on the thienylenic segment. Moreover the lack of any infrared activity suggests that these excitations are not charged. We believe that this is due to the fact that in T_3B_2 the width of the potential well formed by the three thiophene rings is not large enough to accomodate bipolarons. No localization effects of charged excitations are observed within the short sequences, in agreement with theoretical calculations. [12] On the basis of these considerations we suggest that the electronic features of the T_3B_2 correspond to the self trapped states of a copolymer rather than those peculiar of a superlattice structure.

In conclusion, we have presented novel data on the optical properties and photoexcitations of regular block copolymers made of alternating thienylenic and phenylenic moieties with the aim of observing possible localization effects indicative of the presence of a regular alternation of potential wells separated by barriers, which is peculiar of a superlattice structure. Even though the low molecular weigth obtained from the polymerization reaction probably prevents the existence of a long range superperiodicity along the chain, Raman and optical data indicate that the thienylenic section of the copolymer behaves indeed as a potential well. Photoinduced spectra suggest that these potential wells can accomodate bipolarons (which have been demonstrated to extend over at least four chemical units)[12] only if the number of adjacent thiophene rings is large enough. Our experimental data indicate quite unanbiguously that this situation is reached in T_6B_2 but not in T_3B_2. It appears that block copolymers consisting of at least five-six units on each block are required to produce localization effects peculiar to a true polymeric superlattice. This requirement poses severe limitations to the chemical synthesis of the building blocks of the copolymers since long conjugated segments are usually insoluble.

REFERENCES

1. T. A. Skotheim, Handbook of conducting polymers, Marcel Dekker, New York, 1986.
2. T. Yoshimura, Optics Commun. 70, 535 (1989).
3. R.Nötzel and K. H. Ploog, Adv. Mater. 5, 22 (1993).
4. S. Destri, W. Porzio and Y. Dubisky, in preparation.
5. S.A. Jenekhe, Chem. Mat. 3, 878 (1991).
6. S.A. Jenekhe and W.C. Chen, Appl. Phys. Lett. 57, 126 (1990).
7. C. Botta, S. Destri, W. Porzio and R. Tubino, in preparation.
8. G. Louarn, J.-Y. Mevellec, J.P.Buisson and S.Lefrant, Synth. Met. 55, 587 (1993).
9. R. H. Friend, D.D.C. Bradley and P.D. Townsend, J. Phys. D: Appl. Phys. 20, 1367 (1987).
10. G. Lanzani, L. Rossi, A. Piaggi, J. Pal, R. Zamboni and C. Taliani, Chem. Phys. Lett., submitted.
11. Z. Vardeny, E. Eherenfreud, O. Brafman, N. Nowak, H. Schaffer, A. J. Heeger, and F. Wudl, Phys. Rev. Lett. 56, 671 (1986).
12. S. Stafström and J.L. Brédas, Phys. Rev.B 38, 4180 (1988).