

## Doping effects on the polymer-chain structure of poly(3-methylthiophene)

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The C=C stretching Raman shifts and photoluminescence (PL) for poly(3-methylthiophene) (P3MT) are measured at various doping levels by in situ electrochemical Raman and PL spectroscopic techniques. It is found that the doping for P3MT induces the nonlinear excitations (soliton, polaron, bipolaron), but also affects the polymer-chain structure, including the conjugated length and the interchain distance.

### 1. Introduction

One-dimensional polymers have attracted significant scientific and technical interest since it was found that the doped polymers exhibit a dramatic increase in the electrical conductivity. The gap states induced by doping corresponding to solitons [1], polarons and bipolarons [2] have been observed in optical absorption spectra. The doping effects on the electrical conductivity have been extensively studied [3]. But, we think that we should also pay much attention to study the effects of doping on the polymer-chain structure, which is an important factor for the character of polymers.

In this paper, we investigate the effects of doping on the polymer-chain structure of P3MT, including the conjugated length and the inter-chain distance, by in situ Raman and luminescence spectroscopic techniques.

### 2. Experimental

In situ electrochemical Raman and photoluminescence techniques are used. The P3MT film is

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deposited on a platinum working electrode surface under a controlled potential of 1.45 V versus SCE (saturated calomel electrode) in a 0.2M tetrabutylammonium perchlorate/acetone nitrile solution containing 0.1M 3-methylthiophene.

The electrochemical experiments are performed with CV-47 polarographic equipment (BAS Co., USA) or a home-made FA-1 potentiostat. The Raman and photoluminescence spectra are measured with a JY-800 Raman spectrometer, an Ar<sup>+</sup> laser being used as the excitation source.

### 3. Experimental results

We have measured the C=C stretching Raman spectra of P3MT at various electrode potentials by the in situ technique, as shown in fig. 1. It is found that the C=C stretching Raman shift increases as the electrode potential varies from -0.8 to 0.4 V, and decreases with the electrode potential from 0.4 to 0.7 V, as shown in fig. 2. From figs. 1 and 2, we can see that the light doping (<0.4 V) increases the C=C stretching Raman shift and that the heavy doping (>0.4 V) decreases it.

Figure 3 shows the photoluminescence spectra of P3MT at various electrode potentials. The peak position of P3MT PL band obviously shifts

Fig. 1. The C=C potentials: (a) -

towards the electrode potential. In fig. 4, we shift of P3MT light doping (the doping le

### 4. Discussion

We have the chain structure

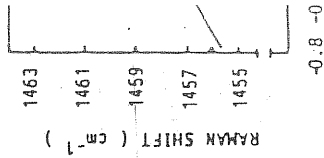


Fig. 2. Variation

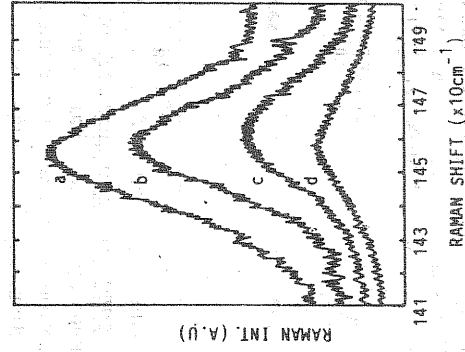


Fig. 1. The C=C Raman spectra of P3MT at various electrode potentials: (a): -0.8 V, (b): 0 V, (c): 0.4 V, (d): 0.7 V, versus SCE.

towards the high energy side with increasing electrode potential, i.e., with increasing doping level. In fig. 4, we notice that the variation of the blue shift of P3MT PL band with doping is small for light doping ( $< 0.4$  V) and that it is very large as the doping level is high ( $> 0.4$  V).

#### 4. Discussion and conclusions

We have theoretically studied [4] the polymer-chain structure (chain length and interchain dis-

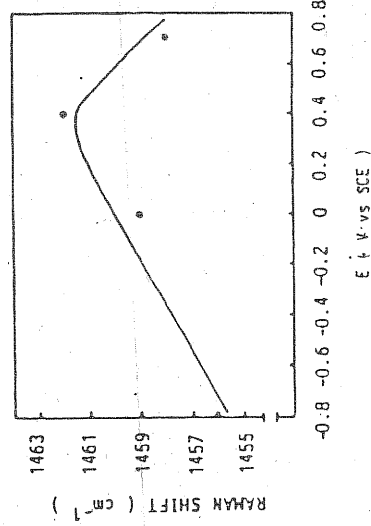


Fig. 2. Variation of the C=C Raman shift of P3MT with the electrode potential.

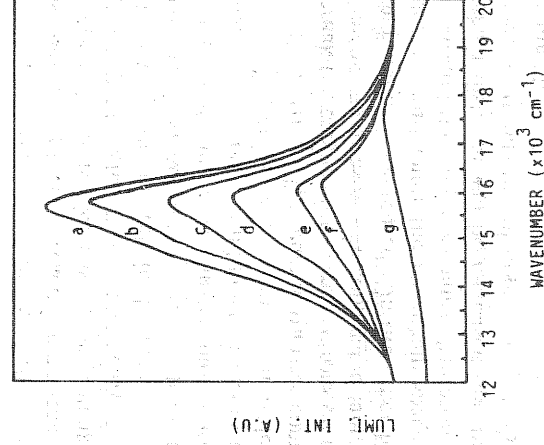


Fig. 3. Luminescence spectra of P3MT at various electrode potentials: (a): -0.8 V, (b): -0.4 V, (c): -0.2 V, (d): 0 V, (e): 0.2 V, (f): 0.4 V, (g): 0.7 V.

tance) dependence of the C=C Raman shift and PL and pointed out that 1) the C=C Raman shift is inversely proportional to the conjugated length of chains and the interchain distance; and that 2) the PL band shifts to high energy side with decreasing conjugated length and increasing inter-

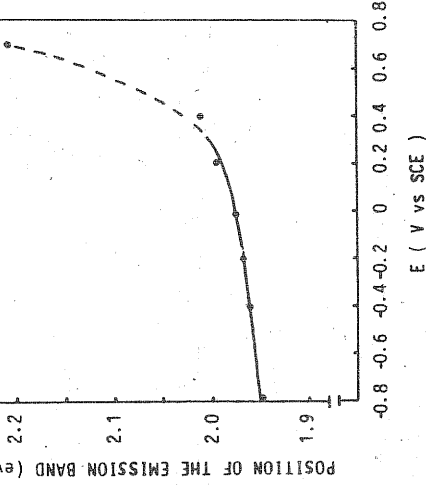


Fig. 4. Relationship between the peak position of P3MT PL band and the electrode potential (doping level).

are measured at the doping for structure, including

electrode surface potential. The Raman shift of the C=C Raman band varies from 1455 to 1463  $\text{cm}^{-1}$  as the potential varies from -0.8 to 0.8 V. The Raman shift of the C=C Raman band is inversely proportional to the conjugated length of chains and the interchain distance; and that 2) the PL band shifts to high energy side with decreasing conjugated length and increasing inter-

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chain Raman shift and PL and pointed out that 1) the C=C Raman shift is inversely proportional to the conjugated length of chains and the interchain distance; and that 2) the PL band shifts to high energy side with decreasing conjugated length and increasing inter-

chain distance of both Raman shifts and PL bands, our experimental results imply that the light doping mainly decreases the conjugated length of P3MT chains and the heavy doping mainly increase the interchain distance.

The relation between the polymer-chain structure and the doping level can be understood as follows. The dopant around polymer chains must form the charge transfer complex in order to induce the carriers. This charge transfer complex will break the conjugation of  $\pi$ -electrons on polymer chains. As a result, the conjugated length of polymer chains is decreased. On the other hand, the dopant must enter the interchain space and arrive around the polymer chains. Therefore, the interchain distance will be increased due to the entrance of an amount of dopant, especially, for heavy doping.

In ref. [5], we have pointed out that the energy gap (and hence, the PL band) of a chain depends

strongly on its length; a smaller energy gap for a longer chain, a larger gap for a shorter chain. In addition, the decrease of the interchain distance will narrow the width of energy band and hence broaden the energy gap, that results in a blue shift of the PL band.

## References

- [1] A. Feldblum, J.H. Kaufman, S. Estemad, A.J. Heeger, T.-C. Chung and A.G. MacDiarmid, Phys. Rev. B 26 (1982) 815.
- [2] T.-C. Chung, J.H. Kaufman, A.J. Heeger and F. Wudl, Phys. Rev. B 30 (1983) 702.
- [3] N. Basesuc, Z.X. Liu, D. Moses, A.J. Heeger, H. Naarmann and N. Theophilou, Nature 327 (1987) 403.
- [4] Bin Hu, Xinyi Zhang, Xurong Xu, Wenbin Zhang, Daike Wang and Shaojun Dong, to be published.
- [5] Bin Hu, Xinyi Zhang, Yingxue Zhou, Changqing Jing and Jisen Zhang, Phys. Rev. B 43 (1991) 14001.