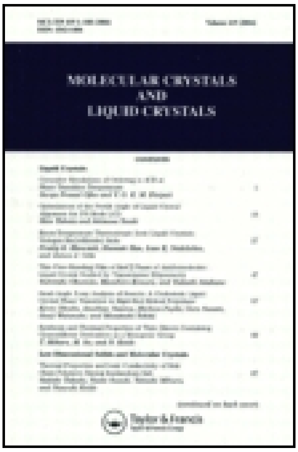

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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To cite this article: X. Q. Yang, T. Inagaki, J. Chen, T. A. Skotheim & Y. Okamoto (1988): An Infrared Reflection Spectroscopy Study of Orientational Behavior in Poly(3-methylthiophene) on a Pt Surface, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 160:1, 261-267

To link to this article: http://dx.doi.org/10.1080/15421408808083021

Mol. Cryst. Liq. Cryst., 1988, Vol. 160, pp. 261–267
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Printed in the United States of America

An Infrared Reflection Spectroscopy Study of Orientational Behavior in Poly(3-methylthiophene) on a Pt Surface

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Infrared reflection-absorption spectroscopy (IRRAS) has been used to obtain the vibrational spectra of thin films of poly(3-methylthiophene) electrochemically polymerized on a platinum surface. Clear orientational effects, with the thiophene rings oriented parallel to the platinum surface, were observed when the thickness of the polymer films were within a few hundred Angstrom.

INTRODUCTION

The electroactive polyheterocycles generated by electrochemical polymerization represent an important class of materials with a wide variety of potential applications.[1–4] Polythiophene and its derivatives are of particular interest because they show considerable chemical and electrochemical stability against moisture and oxygen in both doped and undoped states.[5]

The interaction of these electrochemically polymerized films with electrode surfaces as well as the orientation and structure of the first several layers are of importance for understanding how the polymer films grow. The electroactive properties will depend on the structure of the polymer film. Vibrational (EELS) and thermal desorption spectra (TDS) have been used previously to investigate heterocyclic 5-membered ring molecules such as pyrrole (C_4H_4NH), furan (C_4H_4O) and thiophene (C_4H_4S) adsorbed on Cu(100) at 85–300° K.[6] The thiophene monomer molecule was observed to be weakly π-bonded to the Cu(100) surface with the ring parallel to the surface plane. Very little work has been done on the interfacial problems of polymer films electrochemically deposited on metallic electrodes. A recent NEXAFS study of the electronic and orientational structure of thin poly(3-methylthiophene) (PMeT) films electrochemically grafted on Pt concluded that thin films of undoped PMeT are partially ordered, with the molecular planes oriented predominantly parallel to the electrode surface for films of the order of 100 Å and thinner.[7] By increasing the thickness of PMeT, the orientational effect becomes weaker and vanishes for films a few hundred Å thick.

In this paper we report the first infrared reflection absorption spectroscopy (IRRAS) study of thin PMeT film electrochemically polymerized on Pt. A detailed description of the (IRRAS) technique can be found elsewhere.[8–10] When light is reflected from a flat metal surface, the component polarized perpendicular (s wave) to the plane of reflection (the plane which contains both the incident and the reflected beams and it is perpendicular to the metal surface) undergoes a phase shift of about 180 degrees at virtually all angles of incidence. Hence, the reflected beam will destructively interfere with the incident beam, producing a node at the reflective surface. The component polarized parallel (p wave) to the plane of reflection experiences a phase shift on reflection varying from zero degrees at small incident angles to about 180 degrees at large angles. For grazing incident angle, the net result is an electric field vector polarized normal to the reflecting surface. The electric field vector geometries for transmission and reflection are shown in Figure 1. With grazing incident angle, therefore, only the vibrational modes with a component of the dipole transition moment oriented along the surface normal will be excited. This surface selection rule and the sensitivity to study monolayers on metal surfaces make IRRAS an ideal tool for studying the orientational effects of thin PMeT films on metal electrodes.

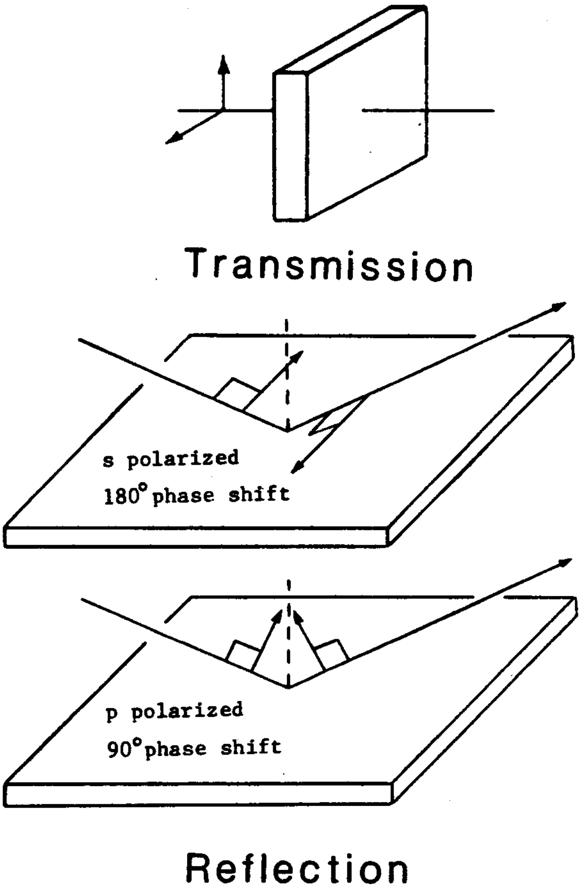

FIGURE 1 Electric field vector geometries for transmission and grazing incident reflection at a metal surface.

EXPERIMENTAL

Films of PMeT were electrochemically polymerized on sputtered Pt electrodes from an acetonitrile solution consisting of 0.5 M 3-methylthiophene, 0.2 M (tetraethylammonium tetrafluoroborate) (TEABF$_4$) with an anodic potential of +1.8 V vs. the saturated calomel electrode (SCE). This resulted in a oxidized blue PMeT film grafted to the electrode surface. The thickness of the film could be controlled by monitoring the electric charge transferred during polymerization using the relationship of 10 Å/(mC-cm^2)[5] as determined with a DEK-

TAK profilometer for films greater than a few hundred Å and extrapolated to thinner films. After polymerization, the potential was reversed to −0.2 V (SCE) to obtain the red reduced semiconducting state. All experiments reported in this paper concern reduced samples. The sample was subsequently rinsed with ethanol and dried in a nitrogen stream. The infrared spectra were taken with a Mattson Cygnus 100 with a room temperature DTGS detector. A modified specular reflection accessory was used. A sample wheel could be turned from outside of the spectrophotometer to interchange the sample and the reference without breaking the purge. The schematic of the grazing incident angle reflection attachment is shown in Figure 2. This improvement reduced the problem of H_2O and CO_2 bands due to the unnormalized background during sample changing. A platinum coated microscope glass slide was used as reference. The sample chamber was purged continuously with nitrogen during the data acquisition. An incident angle of 85° was used for all the samples and 2000 scans were averaged for improved signal-to-noise ratio.

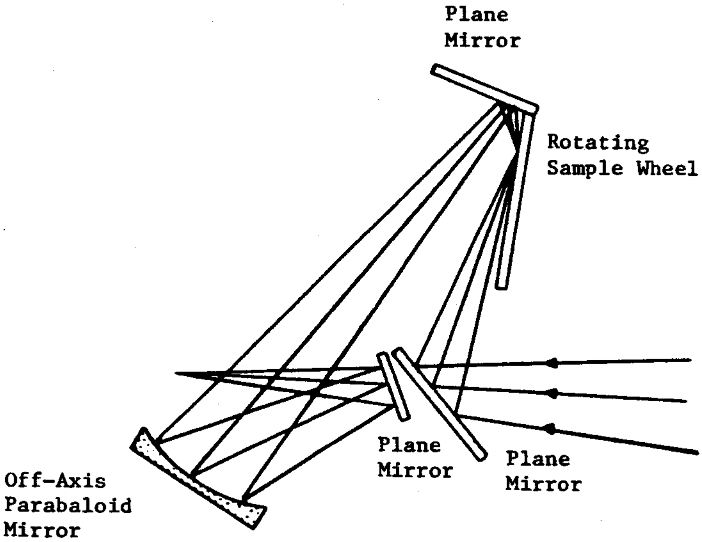

FIGURE 2 Schematic diagram of Grazing Incident Reflection (GIR) attachment.

DISCUSSION

The IRRAS spectra in the frequency range 4000–500 cm^{-1} for reduced PMeT films of thickness 1500 Å, 600 Å and 200 Å with 4 cm^{-1}

resolution are plotted in Figure 3. The absorbance was calculated as log (R_0/R) where R_0 and R is the reflectance of reference and sample respectively.

It is difficult to make detailed assignments of all the absorption peaks in the frequency range between 1800 cm^{-1} to 500 cm^{-1} since very little IR work on these materials have been published. However, the sharp band at 822 cm^{-1} could be clearly assigned to a C-H out-of-plane bending mode at the β position[5,11–13] (see Figure 3), and the peak at 612 cm^{-1} is assigned to the out-of-plane bending mode of the ring.[6] As can be seen from Figure 3, the relative intensity of these two modes increases with decreasing thickness. This is consistent with the 3-methylthiophene rings being aligned increasingly more parallel to the Pt substrate closer to the interface as also observed with NEXAFS spectroscopy.[7] The surface selection rule makes all the modes with dipole moment parallel to the substrate inactive. With the thiophene ring parallel to the substrate, all the in-plane vibrations (in the 1500 cm^{-1} to 900 cm^{-1} range) will be severely suppressed, while the out-of-plane vibrations become more pronounced since their dipole moment is normal to the substrate.

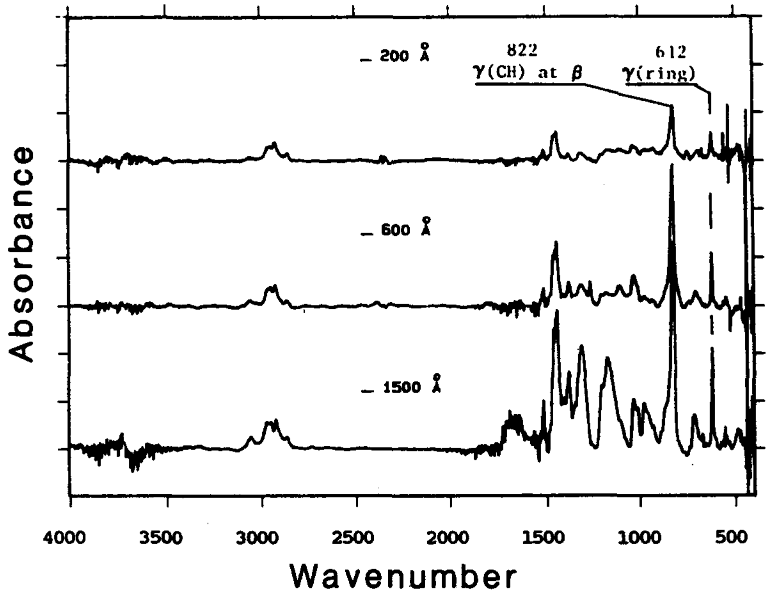

FIGURE 3 IRRAS spectra of undoped poly(3-methylthiophene) with 200 Å, 600 Å, and 1500 Å thickness over the wavenumber range 4000 to 500 cm^{-1}.

TABLE I

Band assignment for undoped poly(3-methylthiophene) in the wavenumber range 3200 to 2800 wavenumbers

Frequency cm^{-1}	Mode	Polarization relative to the plane of the molecular ring
3056	ν (CH) at β Position	parallel
2962	$\nu_a(CH_3)$ in skeletal plane	parallel
2950	$\nu_a(CH_3)$ out of skeletal plane	perpendicular
2920	$\nu_a(CH_2)$	both
2865	$\nu_s(CH_2)$	both

ν Stretch (a, asymmetric; s, symmetric)

The C-H stretching modes (in the frequency range of 3100 cm^{-1} to 2800 cm^{-1}) are well characterized.[14–17] The assignment of these modes are listed in Table I. The spectra of PMeT with thickness 1500 Å, 300 Å and 200 Å are plotted in Figure 4. As can be seen, the 3056 cm^{-1} C-H stretching mode of the β position and the 2962 cm^{-1} in-plane CH_3 asymmetry stretching mode decrease with decreasing thickness. The dipole moment of these two modes are parallel to the substrate if the ring is parallel to the substrate. Combining the result of increasing intensity of out-of-plane bending modes and decreasing

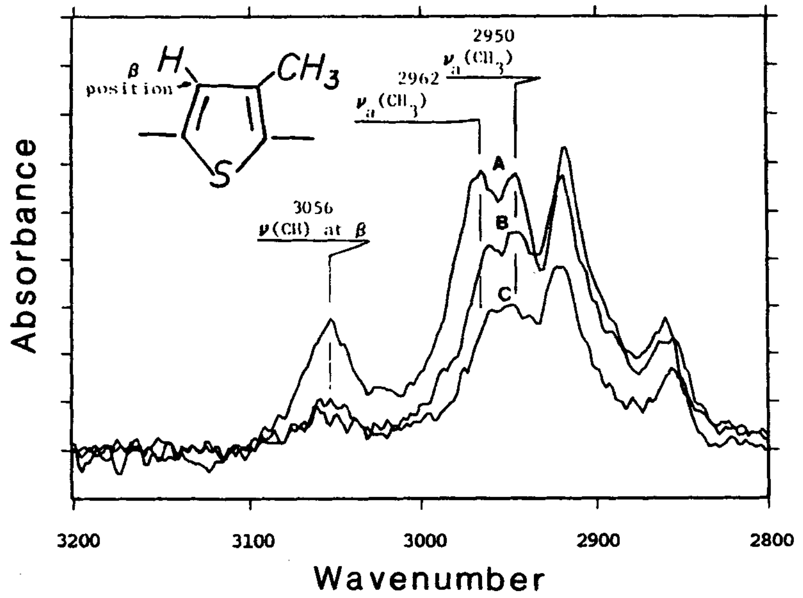

FIGURE 4 IRRAS spectra of undoped poly(3-methylthiophene) with 1500 Å (A), 300 Å (B), and 200 Å (C) thickness over the wavenumber range 3200 to 2800 cm^{-1}.

intensity of in-plane stretching modes when the sample thickness is decreasing, we conclude that the 3-methylthiophene moieties become increasingly aligned parallel to the Pt substrate closer to the interface. Since thiophene monomers are preferentially oriented parallel to the substrate due to the interaction between the π-electron and the metallic substrate,[13] this apparently imposes an ordering on the growing PMeT films. The ordering diminishes with the thickness of the films due to disorder introduced in the growth process. Work is in progress to study this growth process *in situ*.

The C-H stretching modes of CH_2 are common features of the 3-methythiophene IR spectra.[18] It might be due to broken thiophene rings as observed by other investigators as well.[18]

Acknowledgments

The authors would like to thank G. Tourillon for stimulating discussions. This work was supported by the Division of Materials Science, U.S. Department of Energy under Contract No. DE-AC02-76CH00016.

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