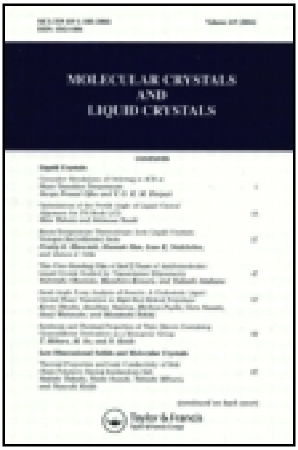

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Yuko Tabuchi, Keisuke Asai, Kenkichi Ishigure, Masahiro Rikukawa & Kohei Sanui (1999): Self-Organization and Opto-Electrical Properties of Poly (3-Alkylthiophene) Langmuir-Blodgett Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 327:1, 131-134

To link to this article: http://dx.doi.org/10.1080/10587259908026797

Mol. Cryst. Liq. Cryst., 1999, Vol. 327, pp. 131-134
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Printed in Malaysia

Self-Organization and Opto-Electrical Properties of Poly(3-Alkylthiophene) Langmuir-Blodgett Films

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(Received June 30, 1998; In final form July 15, 1998)

We examined the self-organized properties of regioregular poly(3-alklylthiophene)s(*HT*-PATs) in Langmuir-Blodgett(LB) films by X-ray diffraction and FT-IR measurements. The *HT*-PATs showed self-organized properties due to their stereoregularity. The pendent decyl groups of *HT*-PDT formed more planar conformation and interdigitated structure. Electrical conductivities of doped *HT*-PATs/SA LB films were dramatically improved compared with random PATs, and *HT*-PDT films showed the highest in-plane conductivities among *HT*-PATs LB films.

Keywords: poly(3-alkylthiophene); Langmuir-Blodgett techniques; self-organization

INTRODUCTION

Poly(3-alkylthiophene)s are of interest with respect to their application to novel opto-electronic devices. McCullough et al.[1] and Rieke et al.[2] have reported that the control of regularity and orientation of poly(3-alkylthiophene) leads to remarkable enhancement of their electrical properties.

These regioregular polymers were also used as excellent tools to investigate the structure-property relationships of conducting polymers. We successfully prepared the Langmuir-Blodgett films containing regioregular poly(3-hexylthiophene) by mixing with stearic acid[3]. We found that the use of regioregular polymers promotes a high level of molecular organization in the LB films. In this study, we prepared the various *Head-to-Tail* poly(3-alkylthiophene)s and investigated the molecular organization and the effect of alkyl chain length on molecular organization and electrical properties of these LB films.

EXPERIMENTAL

Regioregular PATs(R=hexyl(HT), decyl(DT), octadecyl(ODT)) were synthesized according to the Rieke method[2]. All the LB films were constructed by transferring mixed monolayers of *HT*-PATs and SA by the vertical dipping method. X-ray diffraction measurements were performed with a 2θ ranging from 2° to 30° with a CuKα target. FT-IR spectra were taken on a Nicolet Magna-IR system 750 at a resolution of 4.0 cm^{-1} with 2000 accumulations. The incident angle of 80° was used for RA measurements. The in-plane conductivities of the $FeCl_3$-doped films were measured using the van der Pauw method[4].

RESULTS AND DISCUSSION

The molecular organization of *HT*-PATs/SA LB films were probed by X-ray diffraction. Diffraction patterns derived from the self-ordered lamellar structure were observed in the *HT*-PATs/SA LB films. The d-spacing calculated from these patterns of mixed LB films were 18.4 Å(HT), 25.2 Å(DT) and 30.5 Å(ODT). The increase in d-spacing attended the lengthening of alkyl chains. This clearly indicates that the stacks of planar thiophene main chains were uniformly spaced by the alkyl side chains.

Fig.1 displays the transmission FT-IR spectra of *HT*-PATs/dSA(2/1) LB films with 8 layers. Deuterated SA(dSA) was used to independently estimate the orientation of alkyl chains of polymers and SA. The CH_2 and

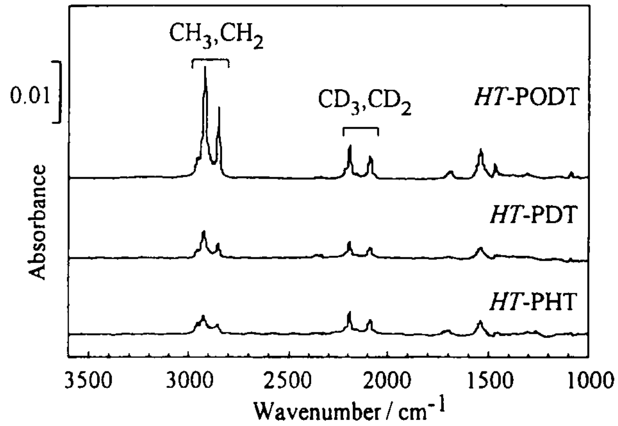

FIGURE 1 Transmission FT-IR spectra of *HT*-PATs/dSA (2/1) LB films.

CH_3 stretching vibrations of the *HT*-PATs are found in 2800-3000 cm^{-1}. According to Umemura's method[5], the tilt angles of hydrocarbon tails of the *HT*-PATs were calculated by comparing transmission with reflection FT-IR spectra. The estimated tilt angles of *HT*-PATs were 58°(HT), 65°(DT), and 39°(ODT), changing as a function of the alkyl chain length. Taking the orientation angle and chain length into consideration, *HT*-PHT and *HT*-PDT exhibited small side-chain tilt angle with better interlayer-mixing.

The mixed *HT*-PATs/SA LB films can be easily converted into electrically conductive materials by doping. Table I displays the conductivities of PATs/SA LB films doped with $FeCl_3$. Conductivities of the *HT*-PATs LB films were dramatically improved and almost 10^3 times higher than those of random PATs. The highest conductivities were observed for *HT*-PDT.

TABLE I In-plane conductivities of doped *HT*-PATs/SA(2/1) LB films.

polymer	Conductivity σ / Scm^{-1}
R-PHT / SA	8.3×10^{-2}
HT-PHT / SA	1.7
HT-PDT / SA	7.6
HT-PODT / SA	7.5×10^{-1}

These results show that self-organized properties and molecular orientation of the *HT*-PATs were affected by the length of alkyl-side chains, and *HT*-PDT formed more stable lamellar structure and showed the highest conductivity.

Acknowledgments

This work was supported by the Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology Corporation.

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