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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Lijun Wang [a], Lin Song Li [a], Lianhua Qu [a], Ran Lu [a], Xiaogang Peng [a], Yingying Zhao [a] & Tie Jin Li [a]

[a] Department of Chemistry, Jilin University, Changchun, 130023, P. R. China

Version of record first published: 04 Oct 2006

To cite this article: Lijun Wang, Lin Song Li, Lianhua Qu, Ran Lu, Xiaogang Peng, Yingying Zhao & Tie Jin Li (1997): A Study on Inorganic Nanoparticles/Amphiphilic Oligomer in Nanoordered Multilayer, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 295:1, 175-180

To link to this article: http://dx.doi.org/10.1080/10587259708042824

*Mol. Cryst. Liq. Cryst.*, 1997, Vol. 295, pp. 175–180
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# A STUDY ON INORGANIC NANOPARTICLES/AMPHIPHILIC OLIGOMER IN NANOORDERED MULTILAYER

LIJUN WANG, LIN SONG LI, LIANHUA QU, RAN LU,
XIAOGANG PENG, YINGYING ZHAO AND TIE JIN LI
Department of Chemistry, Jilin University, Changchun, 130023, P. R. China

Abstract An amphiphilic oligomer, polymaleic acid with octadecanol monoester (PMAO), and its cadmium, lead and copper salts Langmuir-Blodgett (LB) films were prepared. These films possess an ordered structure as determined by X-ray diffraction measurements and FTIR spectroscopy. The long spacing of the films is 5.7 nm. After reaction with $H_2S$, the long spacing increased to 5.8 nm, but an ordered structure was still kept. The nanoparticulate PbS, CdS and CuS multilayers were obtained. From the UV-vis spectrum, it was found that the nanoparticles within PMAO LB films show a larger blue shift of the optical absorption edge than that formed within the stearic acid LB film.

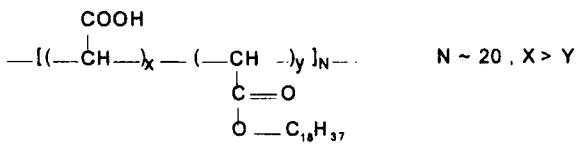


## INTRODUCTION

For the most potential applications of LB films and related systems, the requirements of mechanical, chemical and thermal stability in a wide range of technologies are mandatory.[1-2] Polymers as versatile materials were introduced in the research on LB films.[3] At the same time, the Langmuir-Blodgett method allows one to sequentially deposit a single layer of semiconductor particles within an insulating lattice and then generates an inorganic/organic alternating multilayer films.[4-6] An important goal of all approaches is that the synthesis results in nanosize configurations with a single nanoparticulate monolayer. The most common method to produce Q-state particles in LB films involves the use of long chain carboxylic acids, but instead them into polymers, it will shows more advantage properties in the thermal and mechanical stability.

A series of LB matrix-polymaleic acid with octadecanol monoester and its corresponding salts can be used for the ordered synthesis nanoparticles using in the organized molecular assemblies. The molecular structure is shown below. From the molecular formula, it can be seen that the ratio of carboxylic group to hydrocarbon chain is always larger than one. Several kinds of PMAO with different X:Y ratios (from 2.0:1.0 to 6.0:1.0) have been obtained and all these kinds of PMAO can be

deposited by the LB method which yield typical reproducible isotherms upon compression. In this paper, we will report the results on PMAO salts with X:Y=2.0 in detail.




## EXPERIMENTAL SECTION

The synthesis of the PMAO used in this study has been described in detail elsewhere.[7,8] The PMAO was spread from a chloroform solution at a concentration of approximately $1\times10^{-4}$ mol/L (lateral chain concentration) onto the subphase containing $CdCl_2$ ($3\times10^{-4}$ mol/L)+$NaHCO_3$ ($2\times10^{-4}$ mol/L), $PbCl_2$ ($1\times10^{-4}$ mol/L), $CuCl_2$ ($2\times10^{-6}$ mol/L), respectively. Mayer-Fein technic (Germany) Langmuir trough was used for the equilibrium isotherm studies of the Langmuir layer and the deposition of LB films. The compression expansion speed of the barrier in all experiments was $7cm^2$/min. The isotherms were studies at 19-21 °C. Y-type multilayer films were built up by the vertical dipping method. The substrates for the multilayer were thoroughly cleaned hydrophilic $CaF_2$ and quartz slide when UV-visible and IR measurements were made, whereas silicon wafers were used for small angle X-ray diffraction measurement.

In a vacuum system, CdPMAO, PbPMAO, and CuPMAO LB films were exposed to $H_2S$ (gas) at the pressure of 1 Torr (133.3 Pa). All experiments were carried out immediately after the reaction. X-ray patterns were measured on a Rigaku D/max rA X-ray diffractionmeter. The resulting polymeric multilayer films were characterized by UV/Visible, FTIR spectroscopy, IR spectroscopy were obtained with a Nicolet 5PC FTIR spectrometer and a Shimadzu UV-365 spectrometer, respectively.

## RESULTS AND DISCUSSIONS

### Surface Pressure *vs* Surface Area Isotherms and Transfer Ratio

Typical surface pressure *vs* surface area isotherms for PbPMAO, CdPMAO, and CuPMAO are provided in Figure 1. For PbPMAO, CdPMAO, CuPMAO, the data from the figure indicate collapse pressure of 47, 46, and 38 mN/m, respectively. The extrapolated area per side chain of PMAO is approximately 0.28 $nm^2$ on pure water, it is approximately 0.23 $nm^2$ on the salt subphase. At the surface pressure of 9 mN/m and the dipping speed of 0.7 cm/min, it could not get the desired transfer ratios. However,

the higher dipping speed of 4.0 cm/min cause significant changes in the film behavior, the transfer results would be better. And then, if the surface pressure increased to 18 mN/m, the transfer ratios exceed 0.95. A pure Y-type multilayers can be obtained.

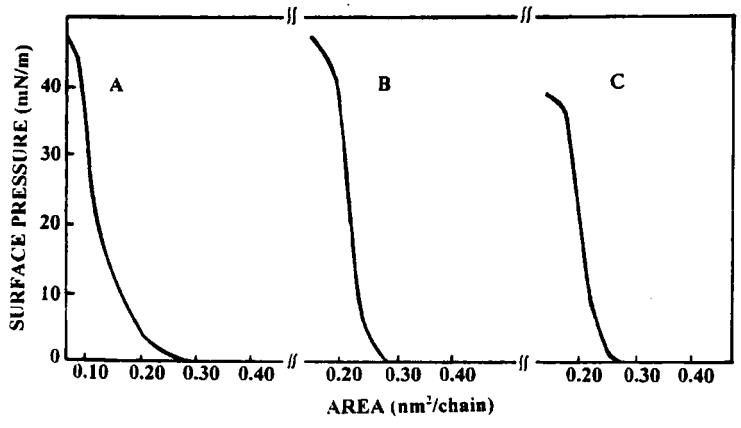



FIGURE 1 π-A isotherms of PMAO. (a) on the surface of $PbCl_2$ solution, (b) on the surface of $CdCl_2$ solution, (c) on the surface of $CuCl_2$ solution.

## X-ray Diffraction of PbPMAO and CdPMAO LB Films

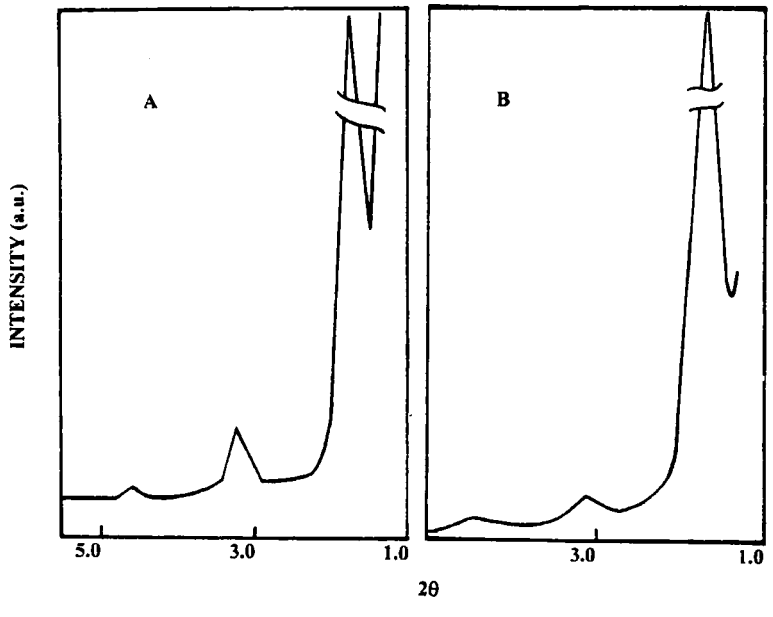



FIGURE 2 X-ray diffraction pattern of (a) PbPMAO, (b) CdPMAO LB films.

The small angle X-ray diffraction patterns of multilayer films of PbPMAO and CdPMAO are shown in Figure 2. From the results of X-ray diffraction patterns, there are three (00*l*) Bragg peaks. It can be calculated from the diffraction pattern that the long spacings are 5.7 nm for PbPMAO and CdPMAO LB films. After the reaction with $H_2S$, the ordered structure was still kept. The long spacings increased to 5.8 nm.

FTIR Spectra of PMAO Salts LB Films Before and After the Reaction with $H_2S$

The infrared transmission spectrum of PbPMAO, CdPMAO, and CuPMAO LB films is shown in Figure 3.

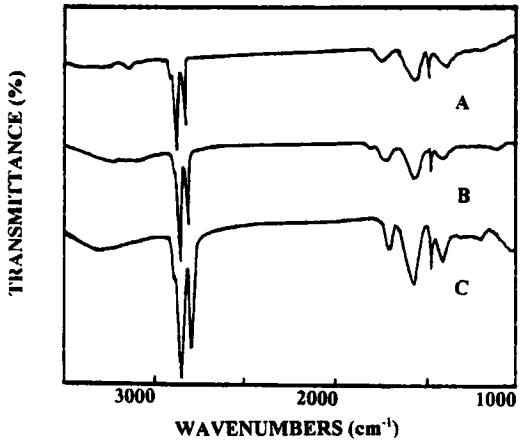



FIGURE 3 FTIR transmission spectra of PMAO LB films (a) PbPMAO, (b) CdPMAO (c) CuPMAO.

The symmetric and asymmetric $CH_2$ stretches (2851 $cm^{-1}$ and 2919 $cm^{-1}$) were observed. The relative greater intensities of these peaks indicate that the alkyl chains are perpendicular to the substrates plane. The 1468 $cm^{-1}$ peak is assigned to the $CH_2$ scissors stretch. The crystal splitting was not seen from this vibration, which shows that the hydrocarbon chains in PMAO LB films do not form the orthogonal arrangements.

In comparison to the FTIR spectra of three different kinds of PMAO salts, we find that the band positions of -COO- asymmetric and symmetric stretch vibrations are different. And also the -COO- frequencies of stretching vibration bands of PMAO salts are apparently different from those of the corresponding stearate salts or other fatty acid salts. The -COO- band positions of PMAO salts LB films are happened to change apparently. The asymmetric stretching vibration frequencies of PbPMAO, CdPMAO, and CuPMAO are seen to shift to higher energy (blue shift), whereas for symmetric

stretching vibration frequencies took place red shifts. The hydrogen bonding is in the form of the metal ion bridges.

Figure 4 show the IR spectra of the Y-type PbPMAO, CdPMAO, and CuPMAO LB films reacted with $H_2S$ at a pressure of 1 Torr for 43 hours and 86 hours, respectively. It can be observed that the intensities of the -COO- asymmetric and symmetric stretching band gradually decrease with the increase of the reaction time. Additionally, the C=O stretching bands are more intense after the reaction than before the reaction with $H_2S$. But the PMAO salts LB films just react with $H_2S$ partly. The reaction degrees (percent rate) are as follows: 70%, 50%, and 40% for CdPMAO, CuPMAO, PbPMAO, respectively.

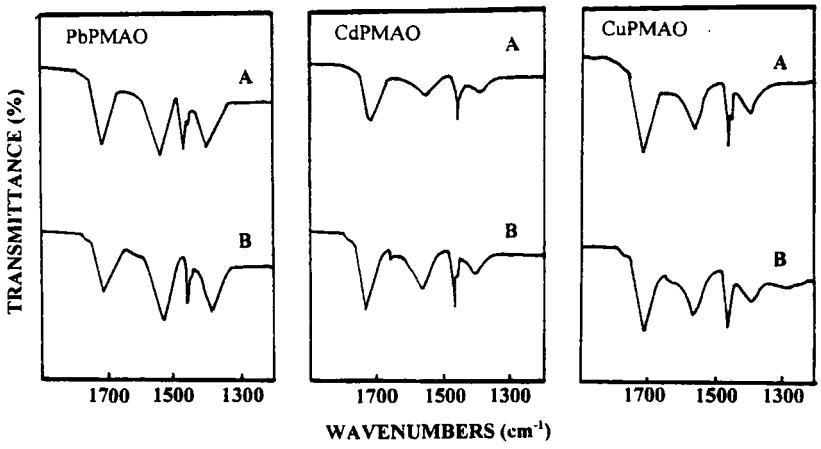



FIGURE 4 FTIR transmission spectra of PMAO LB films reacted with $H_2S$, (a) 43 hours, (b) 86 hours.

UV/Visible Spectroscopy of PMAO Salts LB Films After Reaction with $H_2S$

The preparation of semiconductor particles with quantum size usually produces particles displaying quantum confinement properties, manifested by shifts related to the bulk material in the optical bandgap.

The UV/visible absorption spectra of PbS monolayer prepared by PbPMAO reacted with $H_2S$ for 43, 86, and 135 hours were shown in Figure 5, respectively. By altering the reaction time, there is not obvious shift in the bandgap of the particles. The PbS, CdS, or CuS within PMAO LB films show a much large blue shift of optical absorption edge than that formed within the stearic acid LB films.[9] This implies that the aggregation of the sulfides in the PMAO LB films should be restricted within the small ranges of two-dimensions domains comparison with stearic acid LB films.

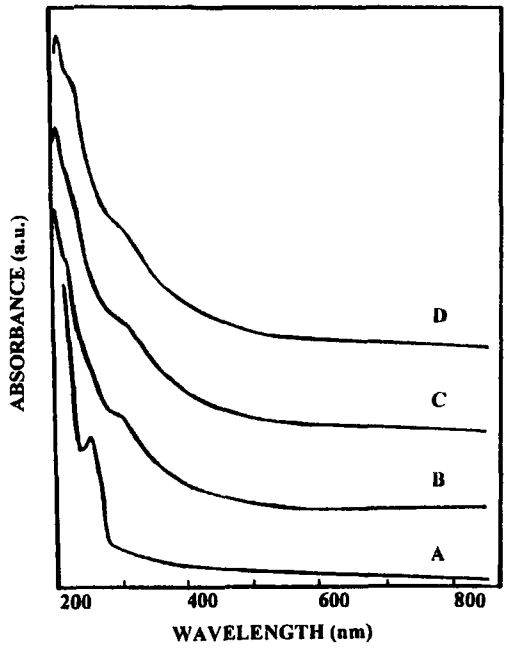



FIGURE 5 UV-vis absorption spectra of PbS monolayer formed by the chemical reaction with $H_2S$. (a) 0 hours, (b) 43 hours, (c) 86 hours, and (d) 135 hours.

Manipulation of the particle size and composition of the nanoparticles in polymerized organic acid films allows for the fabrication of a versatile nanostructured materials. In addition, the size of the nanoparticles could be controlled by changing the ratio between the carboxylic group and the hydrocarbon chain of the polymer.

The authors acknowledge the National Climbing Program and the National Natural Science Foundation of China (NNSFC) for the provision of a financial support.

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