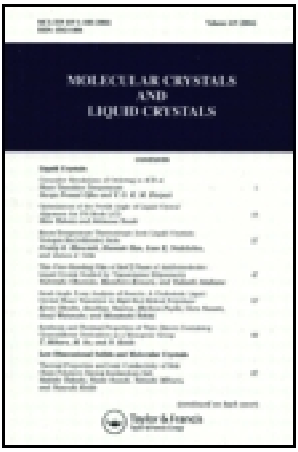


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Annealing Temperature-Dependent Dielectric Properties of $C_{22}$-Quinolinium(TCNQ) Langmuir-Blodgett Films

Tae Wan Kim [a] , Sang-Kug Lee [b] , Dou-Yol Kang [b] & Young-Soo Kwon [c]

[a] Dept. of Physics, Hong-Ik University, 72-1, Mapoku, Seoul, 121-791, KOREA

[b] Dept. of Electrical & Control Eng., Hong-Ik University, Seoul, KOREA

[c] Dept. of Electrical Eng., Dong-A University, Sahaku, Pusan, KOREA

Version of record first published: 24 Sep 2006.

To cite this article: Tae Wan Kim , Sang-Kug Lee , Dou-Yol Kang & Young-Soo Kwon (1995): Annealing Temperature-Dependent Dielectric Properties of $C_{22}$-Quinolinium(TCNQ) Langmuir-Blodgett Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 267:1, 305-310

To link to this article: http://dx.doi.org/10.1080/10587259508034008

*Mol. Cryst. Liq. Cryst.* 1995, Vol. 267, pp. 305–310
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# ANNEALING TEMPERATURE-DEPENDENT DIELECTRIC PROPERTIES OF $C_{22}$-QUINOLINIUM(TCNQ) LANGMUIR-BLODGETT FILMS

TAE WAN KIM
Dept. of Physics, Hong-Ik University, 72-1, Mapoku, Seoul 121-791 KOREA
SANG-KUG LEE, DOU-YOL KANG
Dept. of Electrical & Control Eng., Hong-Ik University, Seoul KOREA
YOUNG-SOO KWON
Dept. of Electrical Eng., Dong-A University, Sahaku, Pusan KOREA

Abstract Frequency-dependent dielectric properties of $C_{22}$-Quinolinium(TCNQ) Langmuir-Blodgett(LB) films were investigated in a frequency range of 10 Hz ~ 13 MHz along a perpendicular direction to the films. The films were heat-treated in a temperature range of 20 ~ 240 ℃. Frequency-dependent dielectric constants show that there are two characteristic dispersions; one is a dispersion occurring near 1 MHz coming from the orientational polarization of the molecules and the other one is probably due to an interfacial polarization below 1 kHz when the annealing temperature is above 80 ℃. The annealing temperature-dependent dielectric constants show that there are two maxima; one at near 80 ℃ and the other one at near 180 ℃. The first peak seems to be related to a disorder of the alkyl chains. The second peak may be due to a chemical structure change of the TCNQ-molecules. Several other methods were employed to understand between the dielectric constants and the internal structure change of the films. DSC (differential scanning calorimetry) data of the $C_{22}$-Quinolinium(TCNQ) molecules shows that there is an endothermic process near 120 ℃ and a weak exothermic process near 180 ℃. Thickness measurement by ellipsometry shows that there is a thickness drop near 100 ℃, which is supposed to be due to a softening of the alkyl chains. The film thickness above 120 ℃ becomes around 20 % of the room-temperature value.

## INTRODUCTION

Semiconductor technology has been successively grown up in miniaturization, reliability, and economic aspect of devices for the last 3 decades. We are, however, currently facing a processing limit in miniaturization of devices even though about $10^{12}$ number of devices per unit area ($m^2$) on a silicon wafer is able to be produced. Thus, there is a study to develop new materials and new processing techniques. For instance, more than $10^{16}$ number of devices per unit area is needed to produce an artificial intelligent machine like a human brain. This kind of size is a molecular level. Recently there is a study for a development of devices using organic materials such as a molecular diode, electron-tunneling switch, molecular transistor, FET (field effect transistor), and etc. These molecular-level devices are called the molecular-electronic devices. There are several ways of producing ultra-thin organic films; Langmuir-Blodgett (LB), physical-vapor deposition (PVD), chemical-vapor deposition (CVD), molecular-assembly method, and so on. The LB method is becoming popular among these methods, because this one has the advantage in its simplicity of the system, easy control of thickness and orientation of the molecules, and low costs.[1] Even though there is a weakness such as a mechanical strength, this kind of problem is expected to be solved sooner or later.

A compound of TCNQ-complex is, in general, well-known as a good conductor, and there is a material with a conductivity of around $10^2$ S/cm.[2] We have been studying physical properties of the $C_{22}$-Quinolinium(TCNQ) LB films such as the anisotropic electrical conductivities, temperature dependent current-voltage (I-V) characteristics,[3] and UV/visible (300 ~ 800 nm) absorption depending on the annealing temperatures (20 ~ 240 ℃). This paper presents the results of the annealing temperature-dependent dielectric properties of the $C_{22}$-Quinolinium(TCNQ) LB films in a frequency range of 10 Hz ~ 13 MHz. To supplement the dielectric properties of the films, DSC (differential scanning calorimetry), and ellipsometry measurements were carried out as well.

## EXPERIMENTAL

### Preparation of the Specimen

Optical microscope slide glass (76×26×1mm) was used as a substrate. Its surface was made to be hydrophilic by cleaning ultrasonically three times in an aceton and ultra-pure water ( ~ 18 MΩ·cm), and then dipping in a $H_2SO_4$ solution saturated by $K_2Cr_2O_7$ for 12 hours. It was rinsed again in an ultrasonic cleaner (Branson 2400) three times for 40 minutes each and then dried in an oven. Aluminum electrodes were vacuum-deposited on the substrate and then the Z-type LB films were made.

Optimum conditions for a manufacture of the LB films were obtained from a $\pi$-A isotherm, relating a surface pressure $\pi$ and an effective area A occupied by one molecule on a subphase. The ultra-pure water was used as the subphase. Since the $\pi$-A isotherm depends not only on the kinds of molecules but the environments of surroundings, it was studied by varying a temperature of the subphase, pH, compression speed and so on. The $\pi$-A isotherm and the films were made using Kuhn type apparatus (Kyowa, HBM-H) which has a trough area of about 570 $cm^2$. The film deposition was carried out under the surface pressure of 45 mN/m at room temperature. And then top aluminum electrodes were vacuum-deposited again. An area of the electrode is 9 $mm^2$.

## Measurements

DSC (Stanton Redcroft DSC 700) measurements of the $C_{22}$-Quinolinium(TCNQ) molecules were done in the temperature range of 20 to 220 ℃. Thermal annealing was performed in air with a heating rate of 2 ℃/min. Frequency- dependent dielectric constants were measured using HP 4192A LF impedance analyzer. Conductance G and susceptance B were measured at each frequency and then complex dielectric constants $\varepsilon^*(\omega) = \varepsilon' - i\varepsilon''$ of the specimen were calculated using the following equations.

$$\varepsilon' = \varepsilon_\infty + \frac{1}{\omega\varepsilon_0}\left(\frac{d}{A}\right)B$$
$$\varepsilon'' = \frac{1}{\omega\varepsilon_0}\left(\frac{d}{A}\right)G \tag{1}$$

Here, $\omega$ is an angular frequency, $\varepsilon_0$ is a dielectric permittivity of vacuum, d and A are the thickness and the area of the electrode respectively. The thickness d of the film was measured by ellipsometry (Gaertner L116C, $\lambda$=632 nm). For the thickness measurement, several 10 layered LB Films were made on a silicon-wafer substrate.

## RESULTS AND DISCUSSION

Figure 1 shows a DSC data of the $C_{22}$-Quinolinium(TCNQ) molecules at a heating rate of 2 ℃/min. There is a strong endothermic process near 120 ℃ and a weak exothermic process near 180 ℃. The endothermic process near 120 ℃ seems to be due to a softening of the alkyl chains, and this agrees to a result of thickness measurement which will be described later. The exothermic process near 180 ℃ seems to be related to a decomposition of TCNQ molecules, which was confirmed by UV/visible absorption spectra and FTIR measurement. The UV/visible absorption spectra show that there is a peak at 494 nm, which is from the absorption of TCNQ molecules. When the films were heat-treated to near 180 ℃, this peak was disappeared. The FTIR measurement also shows that the TCNQ peak at 2181 $cm^{-1}$ disappears near this temperature range. We are going to publish the optical properties later.

Figure 2 is the thickness and the refractive index of the $C_{22}$-Quinolinium(TCNQ) LB films depending on the annealing temperatures measured by ellipsometry technique. Figure 2(a) shows that the thickness of the one monolayer is around 38 Å at room temperature. The thickness decreases slowly as the temperature increases, and there is an abrupt drop near 100 ℃. The thickness at 120 ℃ becomes 20 % of the room-temperature value and it stays almost constant upto

240 ℃. A reason of thickness drop near 100 ℃ may be due to a disorder of the alkyl chains as they become soft. The corresponding refractive index is shown in figure 2(b). The room-temperature value of the refractive index is about 1.6, which is similar to that of fatty acid. As the annealing temperature increases, its value is almost constant up to around 80 ℃ and then increases to the value of about 2.7.

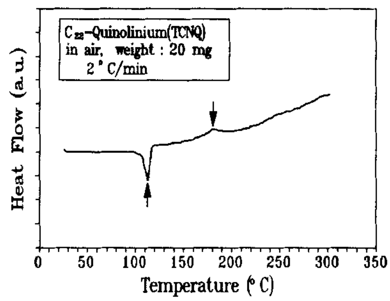


Figure 1 DSC measurement of the $C_{22}$-Quinolinium(TCNQ) molecules.

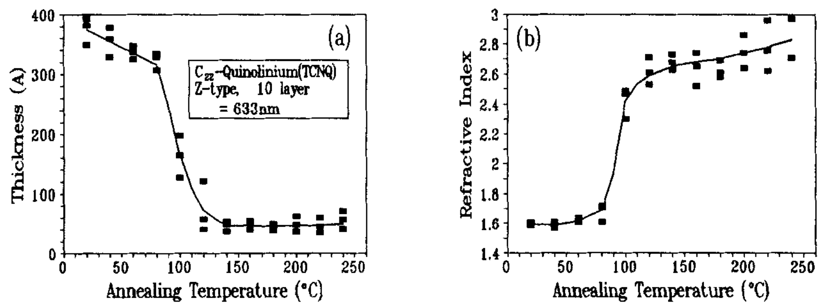


Figure 2 The annealing temperature-dependent thickness and refractive index of the $C_{22}$-Quinolinium(TCNQ) LB films using ellipsometry measurement.

Frequency-dependent complex dielectric constants are shown in figure 3 measured at several annealing temperatures in the range of 20 ~ 220 ℃. Figure 3(a) shows that a real part of dielectric constant $\varepsilon'$ is about 6.5 in the low-frequency range at room temperature and is decreasing slowly upto $10^5$ Hz or so. It decreases abruptly near 1 MHz. A dielectric dispersion of the orientational electric polarization seems to be occurred in this frequency range. The corresponding imaginary part of dielectric constant $\varepsilon''$ shows a peak near 1 MHz. A general behavior of the annealing temperature-dependent dielectric constant is as follows. As the annealing temperature increases, the dielectric constant generally increases upto ~ 80 ℃ and then decreases continuously down to 140 ℃. When the temperature increases further, it again starts to increase very slowly. When the annealing temperature is above 80℃, we can clearly see another dielectric dispersion occurring in the low-frequency region below ~ 1 kHz. This can be interpreted in terms of an interfacial polarization. The effect of interfacial polarization seems to be related to the softening of alkyl chains. After the alkyl chains are becoming disordered state near 80 ℃, the interfacial porarization effect is shown up.

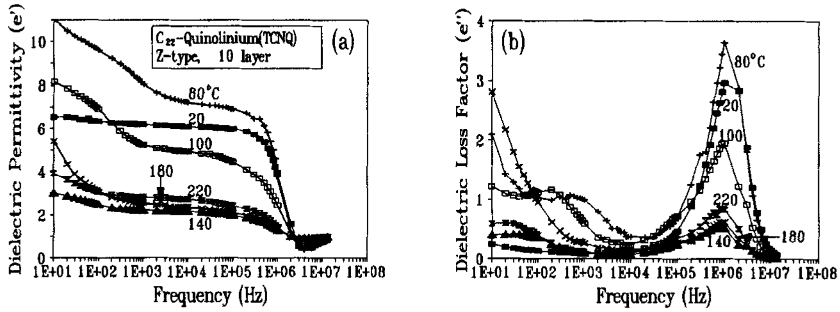


Figure 3 Frequency-dependent complex dielectric constants of the $C_{22}$-Quinolinium(TCNQ) LB films; (a) the real part of dielectric constant $\varepsilon'$, and (b) the corresponding imaginary part of dielectric constant $\varepsilon''$.

Figure 4 indicates the annealing temperature-dependent dielectric constants at several frequencies. It shows that there are two maxama at near 80 ℃ and 180 ℃. These two characteristic temperatures are supposed to be associated with the internal structural and chemical change of the molecules.

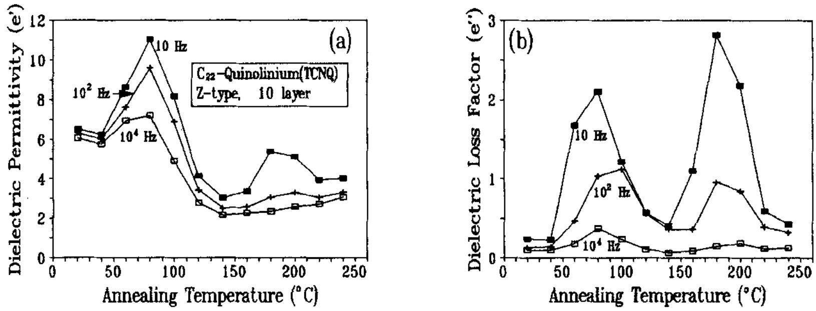


Figure 4 The annealing temperature-dependent dielectric constants of the $C_{22}$-Quinolinium(TCNQ) LB films at several frequencies.

Figure 5 is a Cole-Cole plot representing a relation between $\varepsilon'$ and $\varepsilon''$. In this plot, we can see one or two semicircle depending on the annealing temperatures. The bigger circle is due to the orientational polarization. Using a Debye formula on dielectric relaxation, a relaxation time $\tau$ of the orientational polarization is found to be the order of $10^{-6}$ s.

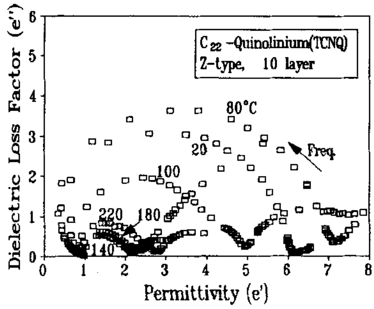


Figure 5 Cole-Cole plot of the $C_{22}$-Quinolinium (TCNQ) LB films on the complex plane ($\varepsilon'$ vs $\varepsilon''$).

## CONCLUSIONS

Dielectric properties of the $C_{22}$-Quinolinium(TCNQ) LB films were investigated depending on the frequency (10 Hz ~ 13 MHz) and the annealing temperatures (20 ℃ ~ 240 ℃). Frequency-dependent dielectric constants show that there are two major dispersions. One is a dispersion of the orientational polarization occurring near 1 MHz and the other is a dispersion of the interfacial polarization below 1kHz. The relaxation time of the orientational polarization is the order of $10^{-6}$ s. The annealing temperature dependence of dielectric constants shows that there are two characteristic temperatures; 80 ℃ and 180 ℃. The behavior near 80 ℃ is related to a disordering of the alkyl chains, and the one near 180 ℃ is supposed to be related to a chemical structure change of the TCNQ molecules.

## Acknowledgments

We appreciate Prof. Woon-Kie Park and graduate student Wan-Shik Cha for helping ellipsometry measurement. This work was supported by a Grant-in-Aid from the Hong-Ik University in 1994 and the Ministry of Science and Technology of Korea.

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