

Structural and electrical characterisation of betaine-type, organic, molecular, thin evaporated films and LB multilayers

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The structure and electrical properties of highly polar indandione-1,3 pyridinium betaine (IPB) derivatives have been studied in vacuum-evaporated thin films and Langmuir–Blodgett (LB) multilayer assemblies. Phase transitions induced by temperature and/or electric field have been observed in LB films of an amphiphilic derivative of IPB.

The LB films of IPB, obtained at room temperature, form a Y-like structure which melts at about 50°C to produce spherical domains, having Z-like structure, which remain stable up to 110°C. Similar phase transitions can be induced by an electric field with $E \geq 2 \times 10^5 \text{ V cm}^{-1}$ at room temperature. In the new Z-like phase of the IPB LB films, the electrical conductivity increases by some five or six orders of magnitude and the activation energy of dark conductivity decreases from $0.18 \pm 0.03 \text{ eV}$ to practically zero.

The vacuum-evaporated IPB films yield low electrical conductivity ($\sigma = 10^{-15} - 10^{-16} \text{ S cm}^{-1}$), whereas in the LB multilayers a notable anisotropy of conductivity is observed. In case of coplanar cells the conductivity increases to $\sigma = 10^{-8} \text{ S cm}^{-1}$. In sandwich-type LB samples the conductivity value is similar to that of the vacuum-evaporated polycrystalline thin films. © 1997 Elsevier Science Ltd. All rights reserved.

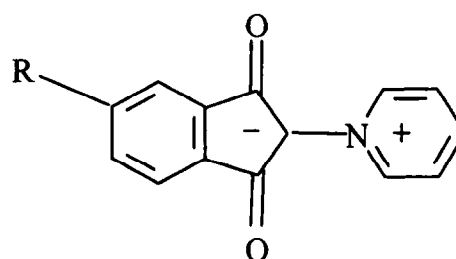
(Keywords: thin evaporated films; Langmuir–Blodgett films; structure; electrical properties; indandione-1,3 pyridinium betaine derivatives)

INTRODUCTION

Polar derivatives of 1,3-indandione betaines are characterised by intramolecular charge transfer^{1–3}. In these molecules asymmetric charge distribution and, consequently, high values of the ground- and excited-state dipole moments are observed^{1,3}. A number of polar derivatives of 1,3-indandione betaines are good photoconductors², particularly the derivative 1,3-indandione pyridinium betaine (IPB) (see *Scheme 1*). This compound yields a ratio of photocurrent (i_{ph}) to dark current (i_{d}) of $i_{\text{ph}}/i_{\text{d}} = \sim 10^3 - 10^4$ ^{11,21}. IPB is also of considerable interest owing to observed non-linear optical effects⁴.

The derivatives of IPB have been studied mainly as vacuum-evaporated thin films. In order to prepare these films by the Langmuir–Blodgett (LB) technique, amphiphilic derivatives of IPB—namely, C17-IPB

molecules with aliphatic ‘tails’ containing 17 carbon atoms (see *Scheme 1*)—were synthesised by Professor O. Neiland’s group at Riga Technical University³.



IPB

where R=H or C₁₇H₃₅

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In this work the structure and electrical properties of both vacuum-evaporated thin films as well as LB multilayer assemblies of IPB are studied and compared.

It has been shown that the electrical parameters of LB films are probably the most sensitive indicators of structural changes occurring in the samples (see Reference 5 and references therein). However, there are a number of purely technical problems concerning studies of the relationship between, for example, electrical conductivity and the structure of LB films, and hitherto such studies have been only fragmentary. One of the main objectives of the present work was comparative electrical and structural investigations of both vacuum-evaporated and LB films. In order to understand the charge carrier transport and trapping processes in these systems the electrical properties were studied by the methods of space charge limited current (SCLC) and, as a result, the local charge carrier trapping state parameters were determined.

The present studies allowed us to elucidate some new, important relationships between the structural and electrical properties of vacuum-evaporated and LB films of the IPB compound. Thus, in LB multilayer films, a phase transition induced by temperature or/and electric field was observed which correlates with a considerable change in the electrical properties of the samples.

EXPERIMENTAL

The IPB vacuum-evaporated films were deposited on quartz, glass or sapphire substrates at an evaporation temperature $T=180\text{--}200^\circ\text{C}$ in a vacuum at $p=10^{-6}$ torr. The evaporation rate (v) was of the order of 0.01 to $0.04\ \mu\text{m}\ \text{min}^{-1}$. The thickness of the layers varied from $L=0.3$ to $1\ \mu\text{m}$.

The amphiphilic compound C17-IPB was deposited on quartz, glass or sapphire substrates by means of the 'step-by-step' LB technique³ at the high-pressure phase of the monolayer at $\pi=45\ \text{mN}\ \text{m}^{-1}$. The monolayer of the amphiphilic C17-IPB molecules was obtained by spreading a solution of C17-IPB ($c=1\ \text{mg}\ \text{ml}^{-1}$) in chloroform on the surface of a water subphase. Dipping of the substrate was performed with different speeds of the downstroke (7.5 to $50\ \text{mm}\ \text{min}^{-1}$) and upstroke ($7.5\ \text{mm}\ \text{min}^{-1}$) directions. The number of dips varied from $n=2$ to $n=30$, and the corresponding number of monolayers (N) of the film was obtained from the deposition coefficient from the deposition diagrams³.

For electrical measurements sandwich-type and coplanar M/IPB/M cells were prepared. In sandwich-type samples Au and Cr were used as bottom electrodes and Al as upper electrodes. In coplanar samples both electrodes were either Au or Cr. In the sandwich-type sample several electrodes were deposited on the film to increase the reliability of the electrical measurements. The area of the electrodes was about $1\ \text{mm}^2$.

The structure of LB multilayer assemblies was studied by means of X-ray diffraction (XRD) measurements. The films were deposited on quartz and glass substrates with number of dips $n=10$ (the corresponding number of monolayers is $N=20$). Experiments were performed with a Rigaku Denki RV300 rotating-anode generator ($40\ \text{kV}$ and $200\ \text{mA}$); Ni-filtered $\text{Cu}\ K_\alpha$ radiation at $\lambda=1.54\ \text{\AA}$ was used. XRD patterns were recorded with a conventional powder diffractometer at various temperatures from 20°C to 120°C . The θ - 2θ reflection geometry was employed⁶.

The morphological parameters of thin films were studied by use of the Brewster angle microscopy (BAM) technique. The LB multilayers of C17-IPB were deposited on a glass substrate in one dip ($N=2$). The homogeneity and domain structure of these layers were registered by NFT BAM equipment⁷.

The absorption spectra of evaporated films as well as LB multilayers in the ultraviolet and visible spectral region from $200\ \text{nm}$ to $800\ \text{nm}$ were recorded with a SPECORD UV-VIS spectrophotometer.

Samples for electrical measurements were mounted in a vacuum cryostat ($p=10^{-6}$ - 10^{-7} torr), which was supplied by a thermoregulator ($T=77\text{--}400\ \text{K}$). Voltage of up to $100\ \text{V}$ was applied and the current, which ranged from $1\ \text{pA}$ to $1\ \text{mA}$, was registered by computer-controlled equipment.

The current/voltage (I/V) characteristics were studied in the regime of monopolar charge carrier injection. From metallic electrodes, in which the Fermi level is below the middle of the forbidden energy gap (E_G) of the molecular crystal, hole injection is usually dominant. In the IPB samples, having $E_G=2.2\ \text{eV}$ [1,2], this condition holds for most high work-function metals such as Au, Al and Cr, which all are typical injectors of holes². The energy parameters of the local charge carrier trapping states were determined by a combination of experimental methods, including conventional SCLC and thermally modulated SCLC (TM-SCLC) (see Reference 8, p. 193). Analytical approximation of the I/V characteristics and the dependence of activation energy (E_a) on applied voltage (U), $E_a(U)$, were based on the assumption of a Gaussian distribution model of local trapping states^{2,8}. These techniques allowed us to determine values for the energy depth of traps (E_t), the dispersion parameter (σ) and the total density of traps for a given set of traps (N_t) in the samples under investigation.

RESULTS AND DISCUSSION

Structural studies of vacuum-evaporated thin films and LB multilayer assemblies

The thin vacuum-evaporated IPB films were of polycrystalline structure and consisted of crystallites of single modification or a mixture of several

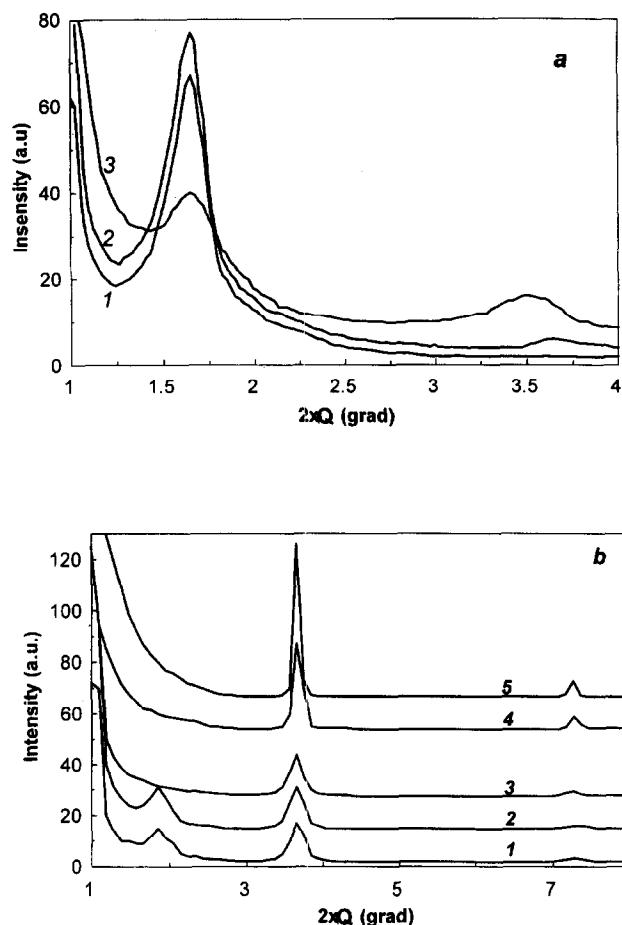


Figure 1 X-ray diffraction patterns of C17-IPB LB multilayers (number of monolayers $N=20$) on a glass substrate at different temperatures: (a) during the first heating process and measured at (1) 20°C, (2) 30°C and (3) 44°C; (b) sample previously heated to 50°C and measured at (1) 20°C, (2) 40°C, (3) 50°C, (4) 90°C and (5) 110°C

modifications, depending on the evaporation conditions⁹. It has been shown by scanning electron microscope measurements that in the vacuum-evaporated IPB films the mean size of crystallites is of the order of $0.2\ \mu\text{m} \times 0.65\ \mu\text{m}$ (for a film thickness of $L=0.2\ \mu\text{m}$). The size of the crystallites increased with increasing thickness of the film and, in the case of $L=1.35\ \mu\text{m}$, their size was of the order of $1\ \mu\text{m} \times 0.7\ \mu\text{m}$.

Figure 1 shows XRD patterns of the C17-IPB LB film, measured at various temperatures. At room temperature the XRD pattern shows only one Bragg peak which corresponds to a lamellar phase with periodicity of the order of $l_1=47.7\text{--}55.8\ \text{\AA}$ [Figure 1a, curve 1]. Since the length of extended C17-IPB molecules is⁴ *ca.* $l_0=33\ \text{\AA}$, these data show that multilayers of Y-like structure are formed with a tilt angle between the molecular axis and substrate surface approximately equal to 50° , in good agreement with reported data of ellipsometric studies³.

The BAM measurements of a fresh sample showed that the LB film had a homogeneous structure [see Figure 2a].

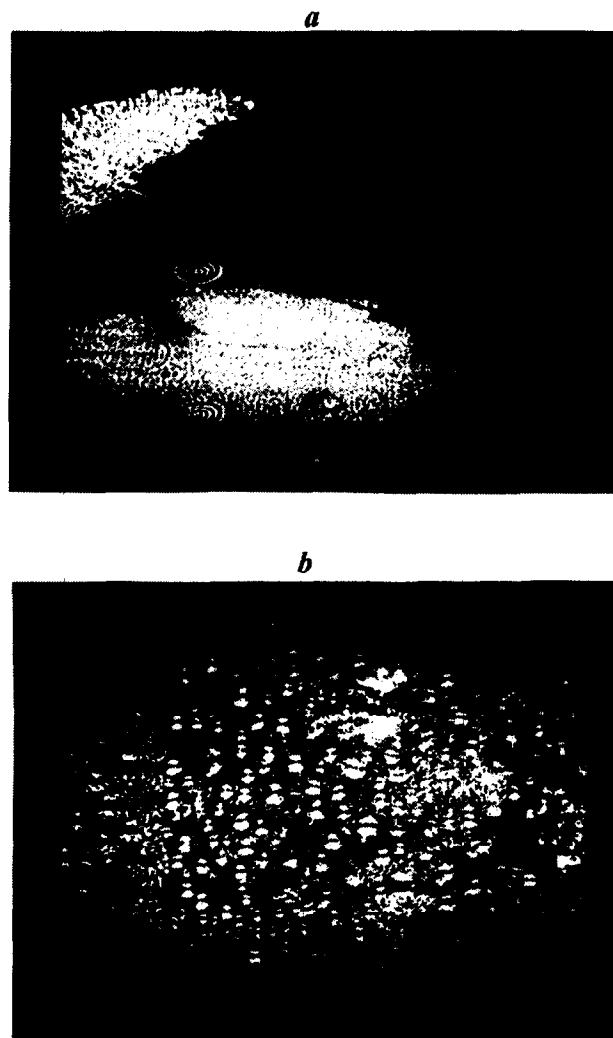


Figure 2 Brewster angle microscopy (BAM) images of the C17-IPB multilayers (number of monolayers $N=2$) on a glass substrate: (a) fresh sample; (b) sample previously heated to 50°C

When the sample was heated, the intensity of the peak in the XRD spectra corresponding to $l_1=52.4\ \text{\AA}$ decreased and new peak at $l_2=24.3\ \text{\AA}$ appeared, which corresponds to the thickness of a single monolayer and most probably confirms the presence of a Z-like structure [see Figure 1a, curve 3]. When a spectrum was measured for a sample that had previously been heated to 50°C, both Bragg peaks appeared [see Figure 1b, curve 1]. In this case it might be assumed that a mixture of both phases is present. Upon increasing the temperature to 50°C, the first peak corresponding to $l_1=52.4\ \text{\AA}$ disappeared, but the second one for $l_2=24.3\ \text{\AA}$ remained [see Figure 1b, curve 3]. The intensity of this peak increased further with temperature up to 110°C [see Figure 1b, curves 4 and 5].

These data confirm the occurrence of a temperature-induced phase transition in C17-IPB LB films. For the low-temperature, Y-like phase the melting temperature is about 50°C. The Z-like structure, which emerges above 50°C, is thermally stable up to 110°C.

BAM measurements show that, after heating to 50°C, the film (in the case of two monolayers) has melted to form droplets and large islands in some places. The film forms spherical domains with intrinsic order leading to optical anisotropy [see Figure 2b]. These droplets might be of monolayer structure. In some LB films of C17-IPB a spherical structure with bright centre regions appeared, which is typical for films that are partly resolved during the following stroke.

As can be seen from Figure 3, heating the C17-IPB multilayer film ($N=20$) to 50°C results in a blue shift of the absorption band in the visible spectral region from $\lambda \approx 410$ nm to $\lambda \approx 380$ nm. It has been shown⁴ that the mean absorbance of a C17-IPB monolayer is about $A_{IL}=0.0085$. By using this value, absorbance measurements in the maximum of the absorption band confirm that the Y-like structure is dominant in the process of film deposition on substrates.

All the above results show that the LB films of C17-IPB form a thermally unstable Y-like structure during deposition which melts at $T=50^\circ\text{C}$ and changes into a new, more stable phase of Z-like structure. These results also demonstrate that thermal stability and the possibility of a temperature-induced phase transition should be taken into account when studying the physical properties of LB multilayers.

Studies of the order-to-disorder transition in LB multilayers have been carried out by a number of authors (see Reference 10 and references therein). Results of investigations into the thermal stability of fatty acid salts show that disordering of the alkyl chains of the amphiphilic 'tail' of the molecules starts at temperatures close to 50°C. By use of the electron diffraction technique it has been shown that, at a temperature range from room temperature to 80°C, fatty acid LB monolayers¹¹ undergo a temperature-induced random tilt orientation disorder, or bending of chains (so-called 'gauche' bonds). At higher

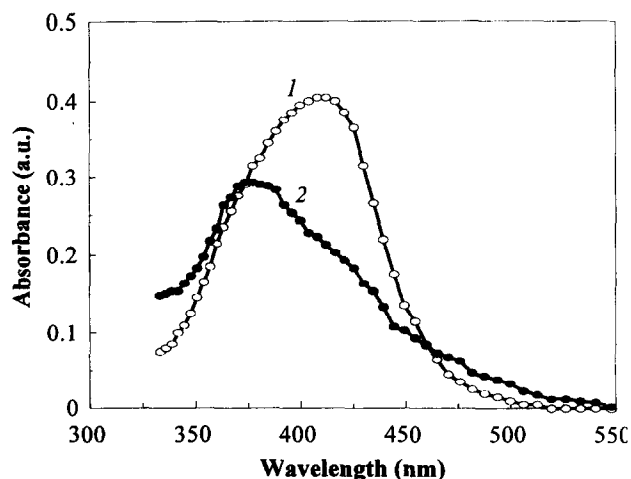


Figure 3 The absorption spectra of the C17-IPB LB multilayers (a) before and (b) after heating to 50°C. Number of monolayers $N=20$

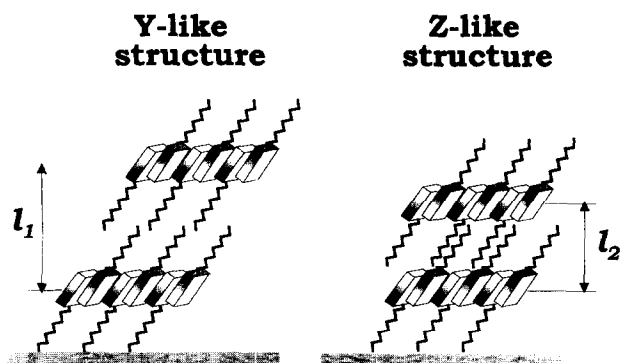


Figure 4 Schematic model of structural transition from Y-like to Z-like structure in the C17-IPB LB multilayer.

temperatures the kinks and jogs are probably distributed along the chains. In LB films of 2-docosylamino-5-nitropyridine, also at temperatures above 55°C, thermally induced phase transition has been observed and is connected with the growth of a new phase, the phase that was initially deposited phase vanishing¹². One may conclude that the thermal stability of LB multilayers is not only dependent on the interaction between alkyl chains but also on the nature and polarity of the head groups and the interaction between them.

In order to interpret the X-ray diffraction data we suggest a hypothetical phase transition model of the C17-IPB films, as shown in Figure 4. This model describes reasonably well how the initially deposited LB film of Y-like structure and period $l_1=52.4$ Å changes into a new phase with decreased period, $l_2=24.3$ Å, and corresponding Z-like structure.

Potential curves of the interaction energy of C17-IPB molecules, calculated by means of quantum chemical molecular orbital CNDO methods, show¹³ that energetically the most favourable configuration of molecules is with antiparallel orientation of the dipole moments of the 'heads' of every molecular pair. During multilayer deposition the Y-like structure, where the 'heads' of molecules are packed in a single layer with antiparallel dipole moments (see Figure 4), is most probably metastable. According to the proposed model, in the process of phase transition the molecular layers are shifting closer and form a more dense and stable Z-like structure. The phase transition shown in Figure 4 also explains the blue shift and decrease in intensity of the absorption spectra of C17-IPB (see Figure 3). It may be caused by an increased repulsive effect between the dipole moments of 'heads' of similar orientation in neighbouring layers (see Figure 4).

Electrical properties of vacuum-evaporated films

Figure 5a shows typical I/V characteristics of evaporated IPB films in a sandwich-type configuration with Au (bottom) and Al (upper) electrodes. The I/V characteristics are superlinear, which indicates

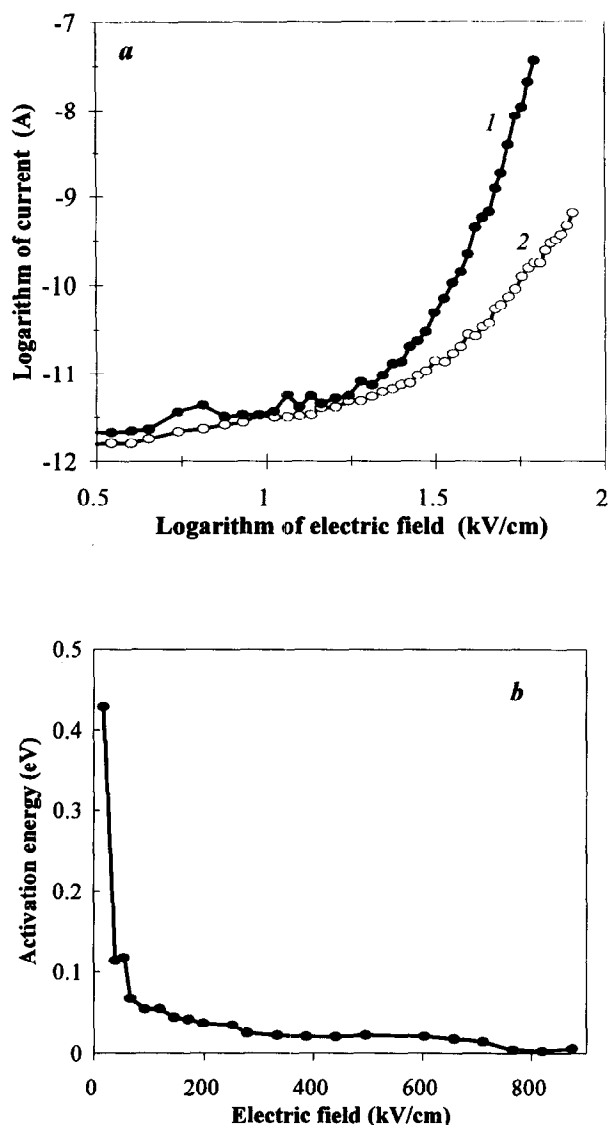


Figure 5 (a) Typical I/V characteristics of thin, vacuum-evaporated IPB films in a sandwich-type Au/IPB/Al cell on log–log scale. Sample thickness $L=0.7\ \mu\text{m}$; injection of holes from (1) Au electrode and (2) Al electrode. (b) Typical activation energy dependence on electrical field, $E_a(\epsilon)$. Injection of holes from Au electrode, temperature range $T=-7$ to 27°C ; film thickness $L=0.3\ \mu\text{m}$

formation of the SCLC regime typical for molecular materials with high resistivity as a consequence of hole injection from a metallic electrode. These I/V characteristics demonstrate a high asymmetry of the current which is dependent on the conditions of injection of charge carriers from the bottom Au or the upper Al electrode. In the case of hole injection from the bottom Au electrode, superlinear I/V characteristics appeared at lower electric field values ($\epsilon \geq 3 \times 10^5\ \text{V cm}^{-1}$) compared with hole injection from the upper Al electrode ($\epsilon \geq 1 \times 10^6\ \text{V cm}^{-1}$). This means that the current is actually limited by a contact barrier in the case of hole injection from the Al electrode. Such behaviour is typical for Al electrodes since they easily form a thin Al_2O_3 layer.

At low electric fields, when the current obeys Ohm's

law, the specific electrical conductivity (σ) of the material may be estimated. The experimental results show that IPB compound is a high-resistivity material, with a specific conductivity equal to $\sigma=10^{-15}$ – $10^{-16}\ \text{Scm}^{-1}$. The superlinear shape of the I/V plot on a log–log scale confirms the presence of sets of charge carrier trapping states of Gaussian distribution^{2,8}. The approximation equations of conventional SCLC theory with Gaussian distribution can thus be applied for estimation of the energy parameters of the sets of trapping states². We also applied the TM-SCLC method, which provides a higher resolution, for obtaining the energy depth for the sets of traps. The dependence of activation energy of electrical conductivity on applied voltage, $E_a(U)$, was measured in this regime^{8,14,15}. From the $E_a(U)$ dependence the energy depth of the sets of traps was estimated.

In the case of IPB thin evaporated films, only one distinct set of hole traps was observed from $E_a(U)$ dependences [see Figure 5b]. The maximum E_t of the distribution of this set of traps is situated very close to hole conductivity level (E_h), i.e. $E_t < 0.05\ \text{eV}$, with the total density of traps being $N_t \approx 1 \times 10^{16}\ \text{cm}^{-3}$ and the parameter of distribution $\sigma \approx 0.08$ – $0.13\ \text{eV}$.

Electrical conductivity of LB multilayers

The electrical properties of LB multilayers of C17-IPB were studied in sandwich-type cells and cells of coplanar configuration. Notable anisotropy of conductivity, dependent on the direction of charge carrier transport, was observed. In the case of hole transport through the sample (bulk conductivity), the electrical conductivity value of the LB films was very low and similar to that of evaporated thin films, i.e. $\approx 1 \times 10^{-15}\ \text{Scm}^{-1}$. On the other hand, the electrical conductivity in the in-plane direction of the LB films was about seven orders of magnitude higher: $\approx 1 \times 10^{-8}\ \text{Scm}^{-1}$. In all cases superlinear I/V characteristics were observed. A similar behaviour of electrical conductivity has also been reported in LB multilayers of anthracene derivatives¹⁶, where superlinear I/V characteristics of the SCLC regime were observed and the value of in-plane conductivity exceeded that in the direction perpendicular to the layers by a factor of 10^8 .

Furthermore, we studied the influence of phase transition induced by temperature and electric field in LB films (see Figure 4) on their electrical conductivity in sandwich-type Au/C17-IPB/Al cells. Figure 6 shows the current dependence on temperature of the LB film at a constant electric field of $\epsilon \approx 2 \times 10^5\ \text{V cm}^{-1}$. As can be seen from Figure 6, the value of current increased drastically by more than five orders of magnitude at $T=21^\circ\text{C}$. We believe that this step-like increase in the electrical conductivity of the sample is directly connected with the phase transition from Y-like to Z-like structures described above.

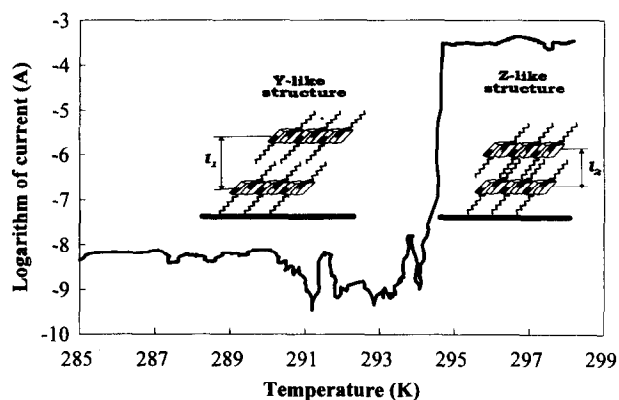


Figure 6 The dependence of current on temperature for the sandwich-type cell Au/C17-IPB/Al. Number of monolayers $N=24$; applied electric field $\varepsilon=2\times 10^5 \text{ V cm}^{-1}$

In our measurements we have discovered that this phase transition is determined both by temperature and electric field. In the absence of the electric field the phase transition occurs at $T=50^\circ\text{C}$, whereas the transition temperature decreases linearly with increasing electric field value. This dependence is shown in Figure 7, where the phase transition temperature is shown to be dependent on the normalised voltage per monolayer.

This interesting dependence may be illustrated by the I/V characteristics of a C17-IPB LB film obtained by three repeated cycles of measurements at room temperature (see Figure 8). The first measurement yields superlinear I/V characteristics, representing a typical SCLC dependence caused by trapped charge carriers (see Figure 8, curve 1). The I/V characteristics of the second cycle of measurements (see Figure 8, curve 2) show enlarged conductivity which increases sharply at $\varepsilon > 2\times 10^5 \text{ V cm}^{-1}$ and indicates that the phase transition has taken place. This conclusion is confirmed by the I/V characteristics of the third cycle of measurement (see Figure 8, curve 3): a considerably higher conductivity is now reached and the I/V plot becomes a linear, Ohmic one.

Thus, the phase transition can be manipulated either by temperature or electric field. However, it should be emphasised that this phase transition is irreversible. The Z-like structure is obviously more stable than the initial Y-like structure.

Thermal activation energy of conductivity of LB multilayers

The activation energy dependence on applied voltage [$E_a(U)$] for the initial phase of a structural sandwich-type C17-IPB multilayer has a quite different character than that for evaporated IPB thin films [compare Figure 5b and Figure 9a, curve 1]. As may be seen from Figure 9a, curve 1, the $E_a(U)$ dependence is more complicated, of oscillatory shape. One should emphasise that the shape of these $E_a(U)$

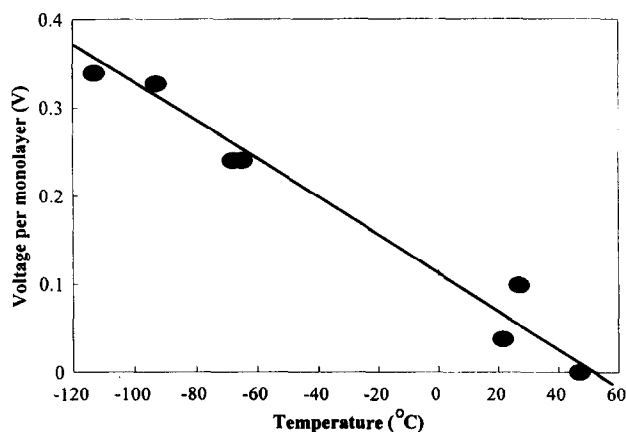


Figure 7 Dependence of the phase transition temperature of the C17-IPB LB films on normalised voltage per monolayer

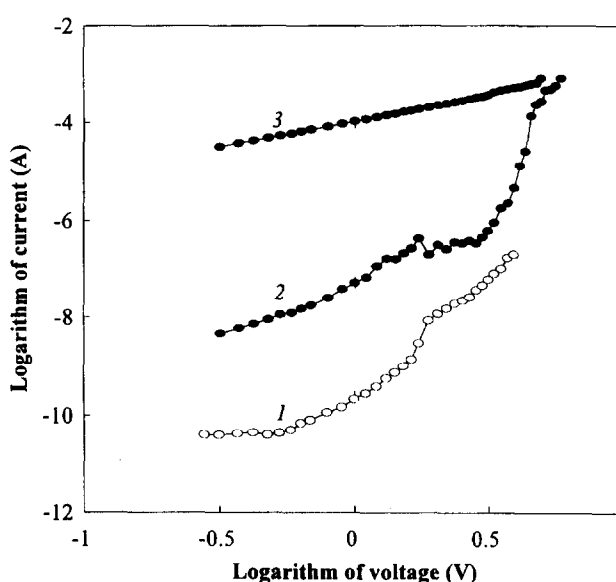


Figure 8 Typical I/V characteristics of the C17-IPB LB multilayer in a sandwich-type Au/C17-IPB/Al cell at room temperature. Number of monolayers $N=38$. (1) First, (2) second and (3) third measuring cycle

dependences is reproducible and is not caused by measurement errors, as shown by error bars. Such reproducible, oscillatory shaped $E_a(U)$ dependences have also been observed for sandwich-type cells of other LB multilayer assemblies, e.g. in vanadyl phthalocyanine LB films¹⁷. Such behaviour has been explained by a spatially non-uniform distribution of total charge carrier trapping states in LB multilayer structures¹⁷. At higher fields, $\varepsilon \geq 5 \times 10^6 \text{ V cm}^{-1}$, the values of activation energy decrease and approach zero, similar to the case of vacuum-evaporated films (Figure 5).

The $E_a(U)$ dependence for the in-plane conductivity of the coplanar cell configuration is of decreasing character [see Figure 9b, curve 1] and from such a type of curve it is possible to evaluate parameters of the trapping states according to TM-SCLC theory. Thus two sets of hole traps, $E_t = 0.45 \pm 0.05 \text{ eV}$ with

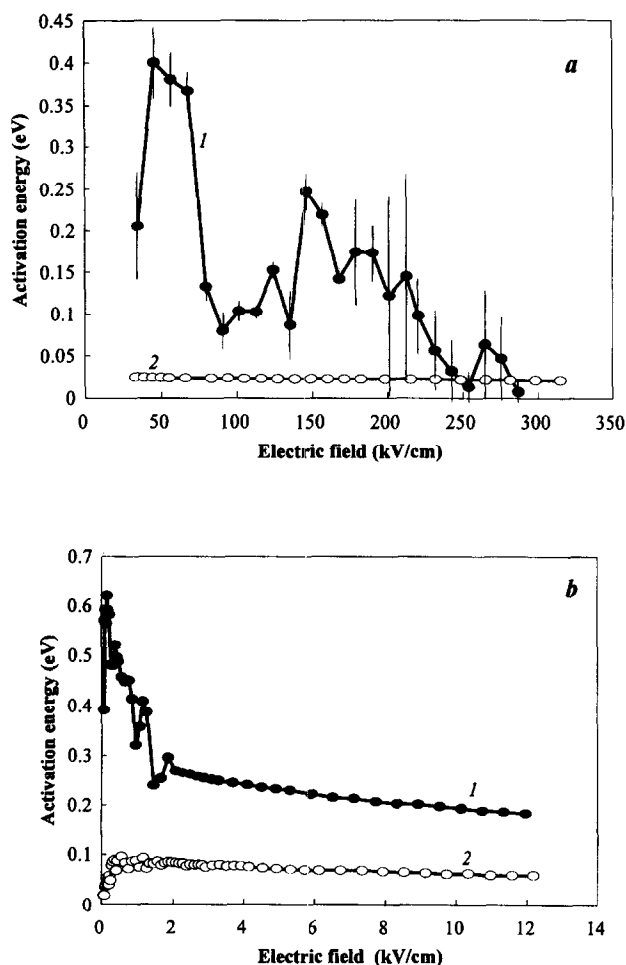


Figure 9 (a) Typical experimental $E_a = E_a(U)$ dependences of the C17-IPB LB films, obtained in the TM-SCLC regime: (a) C17-IPB LB multilayer in a sandwich-type Cr/C17-IPB/Al cell before (1) and after (2) phase transition; (b) coplanar Au/C17-IPB/Au cell before (1) and after (2) phase transition. Interelectrode spacing in the coplanar cell, $d = 80 \mu\text{m}$; temperature range, $T = 7$ to 27°C ; number of monolayers in sandwich-type cell, $N = 38$ and in coplanar cell, $N = 48$

$N_t \approx 3 \times 10^{11} \text{ cm}^{-3}$ and $E_t = 0.18 \pm 0.03 \text{ eV}$ with $N_t \approx 1 \times 10^{17} \text{ cm}^{-3}$, were estimated. The deepest set of traps at $E_t = 0.45 \text{ eV}$ was filled with injected holes at electric field values of $\varepsilon \approx 10^3 \text{ V cm}^{-1}$ and in sandwich-type samples it was not possible to apply such low values experimentally.

In some cases (see Figure 9), at very low electric field, the activation energy (E_a) increased with increasing electric field. As discussed in Reference 14, such dependences may be connected with contact-limited effects at the interface between electrode and organic layer.

The character of the $E_a(U)$ dependences changed drastically after temperature- or electric-field-induced phase transition in the LB film. The value of activation energy both for the bulk and in-plane conductivity of a new, Z-like structure is close to zero and remains practically constant at all values of electric field [see Figure 9a, curve 2 and Figure 9b, curve 2]. This explains the high electrical conductivity

of the samples and the linear Ohmic character of the current (see Figure 8, curve 3).

These drastic changes in the electrical properties of the C17-IPB multilayers may well be explained in terms of the proposed phase transition model (see Figure 4). After the temperature- or electric-field-induced phase transition the LB multilayer transfers from Y-like to Z-like structure and the distance (l) between the molecular 'heads' decreases from $l_1 = 52.4 \text{ \AA}$ to $l_2 = 24.3 \text{ \AA}$. It has been shown that the charge carrier transfer through the quantum wells, formed by the dielectric aliphatic 'tails', occurs via quantum mechanical tunnelling¹⁷⁻¹⁹. As the result of decreased distance l in the Z-like structure, the probability of charge carrier tunnelling via the aliphatic 'tails' increases exponentially and, consequently, the current value increases considerably. Thus, the phase transition model in Figure 4 can explain the dynamics of the changes in electrical and optical properties resulting from the temperature- and/or electric-field-induced phase transition.

CONCLUSIONS

Comparative studies of the structural and electrical properties of polycrystalline evaporated films and LB multilayers of highly polar IPB derivatives demonstrate that there are some similarities between both structural types; however, a number of fundamental differences also emerge. Thus, for example, the specific bulk electrical conductivities of sandwich-type samples of evaporated and LB films are of the same order, i.e. $\sigma = 10^{-15} - 10^{-16} \text{ S cm}^{-1}$. However, owing to their specific multilayer structure, LB films demonstrate a highly expressed anisotropy of electrical properties; i.e. the conductivity along the molecular layers in coplanar LB cells is seven or eight orders of magnitude higher ($\sigma = 10^{-8} \text{ S cm}^{-1}$) than the bulk conductivity.

However, in our opinion, the most important feature observed in the LB films of C17-IPB is the phase transition induced by temperature and electric field from Y-like to Z-like structure. The temperature-induced phase transition may be conventionally interpreted as thermally stimulated transfer from less to more stable structure. On the other hand, it is much more difficult to explain the electric-field-induced phase transition and its correlation with the thermally stimulated transition (see Figure 7). Further studies are required in order to understand this unique effect.

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