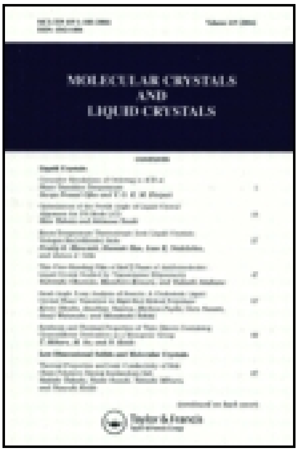

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Electroluminescence in Poly(3,3′Phthalidylidene-4,4′-Biphenylylene)S Films

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To cite this article: Vyacheslay Antipin , Alexey Lachinov & Viktor Kornilov (1994): Electroluminescence in Poly(3,3′Phthalidylidene-4,4′-Biphenylylene)S Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 727-731

To link to this article: http://dx.doi.org/10.1080/10587259408039316

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 727–731
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ELECTROLUMINESCENCE IN POLY(3,3'PHTHALIDYLIDENE-4,4'-BIPHENYLYLENE)S FILMS

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Abstract The paper presents the investigation of the poly(3,3'-phthalidylidene-4,4'-biphenylylene) (PPB) film electroluminescence (EL). EL was found to be of threshold origin, the threshold being 20 V. The voltage varied within a range of 0 V to 100 V. The quantum efficiency was 10%. The results obtained led to a conclusion that EL is due to the recombination processes developing in the polymer proper, for light-emitting accompanying the sample failure belongs to a quite different spectrum area. EL arises when the polymer is in a dielectric state. There is no EL when the polymer is in a conducting state.

At present we are aware of a broad range of polymers displaying electric conductivity, in particular, non conjugated polymers of the poly(phthalidylidenarylene)s (PPA) class. These polymers are interesting in that there is a complex of electronic instabilities observed in their thin layers with a thickness of 1000 nm or less, which results in the appearance of areas (domains) with an abnormally high conductivity[1,2]. The conductivity of these domains was estimated to be up to 10^{11} (Ohm cm)$^{-1}$ at room temperature[3], the temperature dependence of conductivity being typically metallic until the helium temperature[4]. Besides, some of these polymers possess a very efficient photoluminescence[5] visible with a naked eye in natural light.

Non-conjugated polymers of the PPA class - PPB were used for the investigations. The hole injecting electrode was made of InO_2 and the electron injecting electrode was made either of Cu or Cr. The polymer was deposited from the $CHCl_2$ solution on the transparent electrode surface. The polymer layer thickness was 800-1000 nm. The second electrode was deposited by means of thermodiffusion in vacuum. Before the deposition of the second electrode, the polymer film was once again cleaned of the remaining solvent and other impurities by heating it at about 100°C in vacuum for 1 hour.

The polymer sample EL is characterized by the voltage threshold Ut whereupon emitting starts. This threshold value is different at different polarity. The radiation intensity function of the current value is approximately $I_{el} \sim I_c^{1.8}$, where I_{el} - EL intensity and I_c - current passing through the sample. As for possible applications, the quantum efficiency of EL is an important parameter. For the described experimental structure it was 10^{-2}%.

The EL spectral bands coincide with the respective photoluminescence bands (Fig. 1). The situation is quite similar during the EL of poly(p-phenylenevinilene)[6].

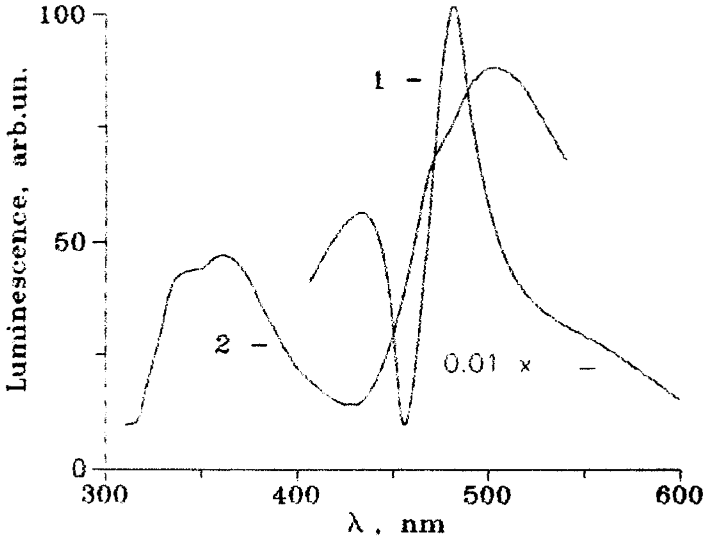

FIGURE 1 Spectral characteristics of PPB film luminescence. 1 - The electroluminescence spectrum. 2 - The photoluminescence spectrum.

Basically, the process of charge transfer of both signs within the sample volume resulting in the recombination emitting can be regarded as intrachannel[7]. Charges move to meet each other and recombine in a certain area of the volume. Such a mechanism is in fact implied by the conventional notion of EL in organic materials.

The channel conductivity of thin PPB films was found earlier[8]. However, different properties of conducting channels was investigated when the polymer was in a highly conducting state. This is why, we knew nothing about the role and properties of channel areas within the polymer film before switching-on or after switching-off. Therefore, the relationship between EL and electron switching of conductivity is very important.

Figure 2 illustrates this relationship. As the field threshold of 8 V is reached, EL is displayed with its intensity growing with the voltage and the current flowing through the sample also increasing. However, with the sample difference of potentials being about 12.5 V, the polymer film switches over into a highly conductive state (HCS), which is indicated in the figure with a dotted line. EL disappears the moment the film is in HCS. The current-voltage dependencies are of the ohmic character, but because of the electron instability of this state, reverse "switching over" to the low conductivity state occurs upon the current reaches a critical value of about 44 mA. The current abruptly drops and the I-V dependence becomes non-linear again. The moment the reverse switching over of conductivity takes place, EL "lights up" again and its intensity grows with the voltage. Hence, there is no EL in the highly conducting state.

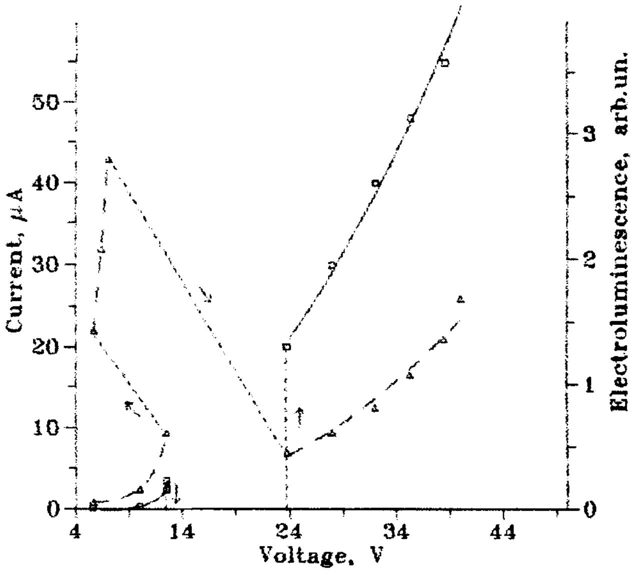

FIGURE 2 Influence of switching into the "ON" - state on light-emitting properties of thin polymer film. Arrows indicate the alternation of voltage. Dashed lines are I-V characteristics, solid lines are EL intensity-voltage characteristics, dotted lines shows the switching sites.

The results obtained indicate that the charge transfer in PPB thin film is limited by the injection of charges from electrodes, at small field values this injection being monopolar. This is proved by a threshold existing in EL and usually associated[7] with the beginning of the process of bipolar injection indispensable for EL. The existence of monopolar injection confirms that electrodes used in the described experiments are not ohmic. The absence of EL in the highly conducting state of polymer can mean that EL originates from those film domains where metal-like channels appear during switching over. On the other hand, the absence of EL in the HCS can be accounted for by shunting the applied electric field by conducting domains thus making it insufficient to induce EL.

However, as shown in Figure 2, near the threshold of the reverse switching over to the low conductivity state, the field surpasses the EL generation threshold. Nevertheless, EL is displayed only after the conductivity has been switched off. This may mean that in the case of HCS, conditions of the electron-hole recombination are not fulfilled, which is probably right if EL originates from domains containing so called conducting channels which in HCS are characterized by the metal-like conductivity.

Hence, another conclusion is that these domains are formed not in the moment of the phase transition to HCS, but appear in the film long before the transition. This is why in these domains the transformation of electron states eventually results in the transition to HCS. This conclusion seems to be rather important, for more often these channels are considered to be formed in the moment of switching over. Of course, it is too early to make a final conclusion concerning the mechanism of EL in the poly(3,3′- phthalidylidene-4,4′-biphenylylene) thin films.

However, it is clear that the discovered EL will not only shed light on the mechanism of the abnormally high conductivity in thin films of some polymers, but also bring us closer to the understanding the whole complex of charge instabilities in such films.

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