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**CARRIER TRANSPORT AND RECOMBINATION IN ORGANIC LAYERS
WITH STILBENE CRYSTALLITES**

MASTER'S THESIS

Photonics and nanotechnology study program

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Acronyms

BGD Bässler's Gaussian disorder.

CELIV Carrier Extraction by Linearly Increasing Voltage.

MSE Mean squared error.

MTR multiple-trap & release.

OFET organic field-effect transistor.

OPA optical parametric amplifier.

OTFT organic thin-film transistor.

PC polycarbonate.

PEPC poly-N-epoxypropyl-carbazole.

PS polystyrene.

PT polythiophene.

PVB polyvinyl butyral.

TOF Time of Flight.

VASE Variable Angle Spectroscopic Ellipsometry.

VRH variable range hopping.

XRD X-ray Diffraction.

1 Introduction

As is well understood in the field of organic electronics and optoelectronics, disorder in organic semiconductor materials significantly affects charge carrier dynamics. Structural and energetic disorder, often manifested through traps and impurities, complicates charge transport and recombination processes by reducing carrier mobility and promoting trap-assisted recombination. Consequently, charge transport parameters in organic semiconductors are typically much lower than those observed in inorganic materials. Despite these limitations, organic electronics and optoelectronics continue to attract strong interest and maintain an important market presence, particularly in applications where conventional silicon-based technologies lack flexibility and mechanical adaptability.

Significant focus is directed to the highest charge mobility offering small-molecule single-crystal semiconductors, however, growing uniform crystals and precisely positioning them for devices is challenging. As a result, organic electronics rely mainly on solution-processing techniques to form highly crystalline thin films with controlled size and orientation [1]. While polymers process well into uniform films, small-molecule semiconductors are difficult to solution-coat due to their low viscosity and poor wetting. A successful strategy is blending them with an insulating binder polymer, which acts as a thickening and wetting agent — producing uniform films without significantly reducing the excellent intrinsic charge mobility of the small molecules [1].

This work investigates hole and electron transport, as well as recombination processes, in blend layers containing a well-known organic molecule *trans*-stilbene and a polymer material. Since single-crystal *trans*-stilbene exhibits exceptional charge transport properties, blending it with a polymer, together with controlled phase separation, represents a promising approach for the fabrication of organic electronic devices. In addition, morphology control within such blend systems may provide a pathway for suppressing charge carrier recombination while preserving efficient transport properties. However, quantitative investigation is necessary to ensure that the blend-processing approach does not significantly compromise the intrinsic transport characteristics of stilbene.

2 Theory and Literature Review

2.1 Charge Carrier Transport in Organic Materials

Charge carrier transport in organic and inorganic semiconductor materials is governed by different mechanisms and thus is described using separate scientific theories. The classical band-like transport theory is expected for highly ordered or disorder-free systems, which mainly consist of single crystalline inorganic semiconductor materials. In contrast, charge carrier transport in majority of organic semiconductor materials, which usually contains energetic and structural disorder, can be described by well known multiple-trap & release (MTR), variable range hopping (VRH) and Bässler's Gaussian disorder (BGD) models [2].

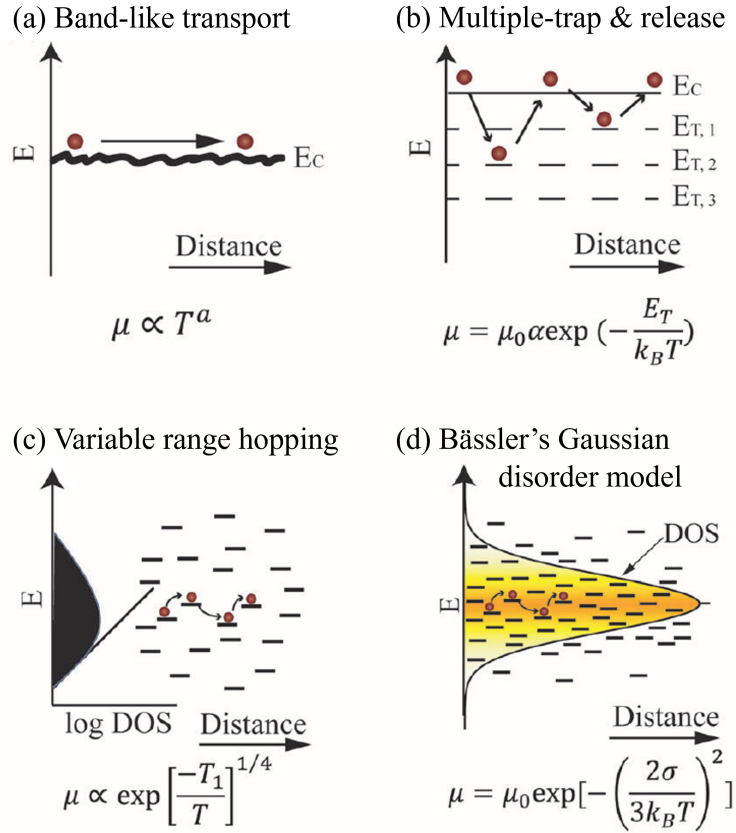


Figure 1. Schematic representation of transport mechanisms for (a) band-like transport, (b) multiple-trap & release (MTR) model, (c) variable range hopping (VRH) model and (d) Bässler's Gaussian disorder (BGD) model. Adapted from [2].

The numerous amount of charge transport models for organic semiconductor materials (just a few mentioned above) is a direct consequence of a vast amount of available said materials. These models usually are specific to a large group of material and are well supported by evidence in different experiments on temperature dependence of carrier mobility [2].

Before exploring any one of the mentioned models in depth, or perhaps skipping this part entirely, the simplest way to explain charge transport in the presence of disorder is to start from the fact that disorder generally localizes the band states found in highly ordered materials [3]. In weakly disordered 3D materials only the states at the band edge are truly

localized. Increasing the degree of disorder progressively localizes the states; at the limit of strong disorder, all states within the band become localized. Transport then operates in the hopping regime with charges jumping between interacting molecules [3]. Refer to **Figure 1c** and **Figure 1d** for the schematic depiction of hopping transport.

Upon describing the hopping transport regime and its origins in organic semiconductor materials, it becomes necessary to discuss the primary quantity characterizing charge transport—carrier mobility [3].

Under applied electric field, and thus the induced drift of carriers within, e.g., an organic layer, the mobility definition becomes the ratio between the velocity, v , of the charges and the amplitude of the applied electric field, E [3]:

$$\mu = \frac{v}{E}. \quad (1)$$

Drift induces a displacement of the average position of a charge, and thus is the effect that dominates (over diffusion, which is seen as a local displacement of a charge around an average position) the migration of the charges across an organic layer in the devices [3].

Naturally it is then a point of interest to determine the mobility dependence on electric field in organic materials, which is also different from the case of single crystal inorganic materials.

The electric-field dependence of mobility in single crystalline materials is typically observed only in high purity crystals and the increase in electric field tends to reduce mobility. Conversely, organic or disordered materials in majority of cases show the opposite dependence—increase in mobility values with increasing electric field. This dependence is typically seen in high electric fields—in the range of 10^4 – 10^6 V/cm, and obeys Poole-Frenkel behavior [3]:

$$\mu(E) = \mu_0 \exp(\gamma\sqrt{E}) \quad (2)$$

where μ_0 is the zero-field mobility, and γ is the temperature dependent field activation parameter.

To further the discussion of carrier mobility, it is essential to consider the typical values found in different organic material categories to establish a baseline for comparison. However, before proceeding, it is necessary to briefly mention that the characterization of p-type or n-type organic semiconductors in literature usually does not reflect the intrinsic ability of the material to transport holes or electrons, but rather indicates how easily these carriers can be injected into the material from traditional electrodes [3]. Therefore, in many organic semiconductors, the electron and hole mobility values are expected to be comparable. Nevertheless, and in the context of ease of carrier injection, materials are usually referred to as hole (electron) transporters when their ionization energy (electron affinity) closely matches

the Fermi level of the electrode material [3].

Now, when talking about carrier mobility values, in best cases, crystalline organic semiconductors (i.e., pentacene) can reach the $0.1\text{--}20\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ value range, while mobility values for amorphous in structure materials usually drop below the $0.1\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [3]. In addition, some π -conjugated polymers can approach the relatively high mobility values, like in the case of polythiophene (PT) derivatives, reaching $0.6\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. On the opposite side, in completely disordered polymer films charge carrier mobility values can be as low as $10^{-6}\text{--}10^{-3}\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [3].

The subsequent chapter (**Chapter 2.2**) discusses in detail a specific case of crystalline small molecule combination with polymer materials for achieving uniform organic layers (films), and, in addition, briefly touches upon key properties related to charge carrier transport, which are not mentioned in this chapter.

2.2 Polymer and Small Molecule Blends

Organic semiconductors can be split into two categories: small molecules or oligomers (usually processed in vacuum) and polymers (often solution-processed) [3]. The semiconducting property of these materials to transport charge is enabled by the conjugation along the backbone (i.e., molecular core), which results in charge delocalization and thus usually higher carrier mobility values [4]. As it happens the most widely investigated organic semiconductor materials (**Figure 2**) do show π -conjugation (conventionally is represented as alternating single and multiple bonds in structural formula). In addition, significant enhancement of charge carrier mobility in organic conjugated materials can also be a result of π - π stacking, which is an arrangement of different molecules connected via van der Waals interactions, that allows charge transport [4].

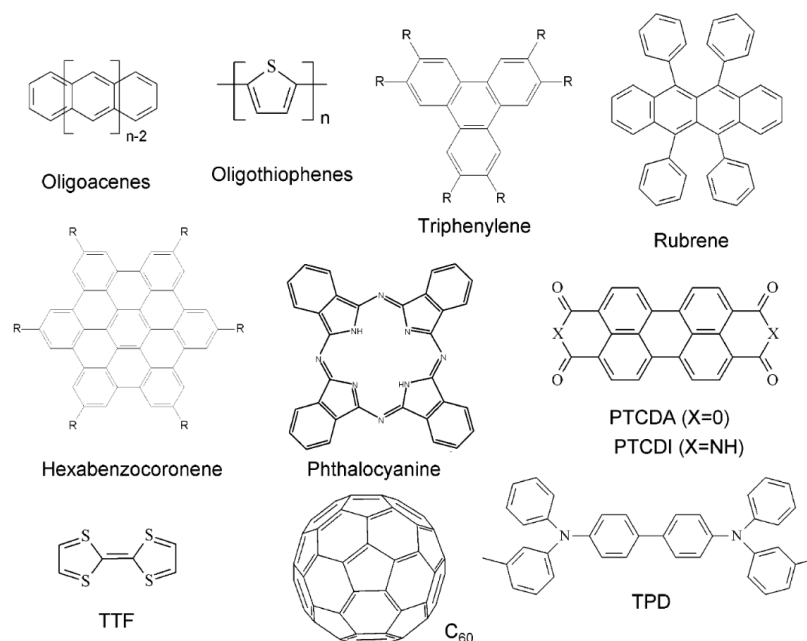


Figure 2. Chemical structures of some of the most studied organic molecular semiconductors [3].

Continuing from the previous paragraph, it is apparent that both intramolecular electronic structure (π -conjugation) and intermolecular morphology (π - π stacking) plays an important role for organic materials in terms of charge carrier transport. When moving from single-component materials to polymer-small molecule blends, the role of intermolecular organization becomes even more pronounced, as thin-film formation governs phase separation, molecular packing, and transport pathways.

Small molecule single crystal semiconductors typically demonstrate the highest mobilities (see **Chapter 2.1**), however, the device fabrication employing these materials faces difficulties of growing uniform crystals and positioning them in a regular manner. Therefore, fabrication of organic electronics is primarily focused on solution processing, such as inkjet printing, spin-coating and so on, to achieve thin films with high crystallinity and controlled crystal size and orientation [1]. Whilst solution processing of polymer semiconductors frequently result in satisfactory thin films, there is significantly more difficulty in preparing thin uniform films by solution coating of small molecule semiconductors, due to the low viscosity and poor wetting. A viable strategy to improve the solution processability of small molecule materials is the incorporation of an insulating binder polymer as a thickening and wetting agent. This approach has been found to produce blend films that do not hinder the intrinsic excellent charge mobility of small molecule semiconductors [1], and in some cases even show significantly better electrical properties for the blend semiconductors in devices such as organic thin-film transistors (OTFTs), when compared with those of neat small molecules [5].

It then becomes essential to identify the basis of outcomes mentioned above, and the evidence points at the thin-film morphology altering factors (few already noted at the start of the page) such as: complex crystallization mechanisms in solution, that may involve initially formed amorphous aggregates, where solvent-solute interactions play a critical role in development of order; the process of phase separation [6]; the miscibility of materials; and the relative rate of aggregation [4]. These factors to some extent are shown in the **Figure 3**, where blend morphology formation is depicted dependent on material miscibility, thus ushering two types of phase separation pathways liquid-liquid (L-L) and solid-liquid (S-L).

Finally, it is important to note that the presence, and type of phase separation (vertical or lateral) does not automatically result in either improved or degraded electrical properties of the device—different blend morphologies (and thus different degree of phase separation) can be either beneficial or detrimental depending on the specific type of device. For example, the vertical phase separation (initiated by the interfacial energy that favors one component over the other at the substrate-semiconductor or the semiconductor -air surfaces) is a necessary condition for obtaining electrical properties of blend semiconductors that are as good as or even better than those of neat small molecules when talking about OTFTs [5].

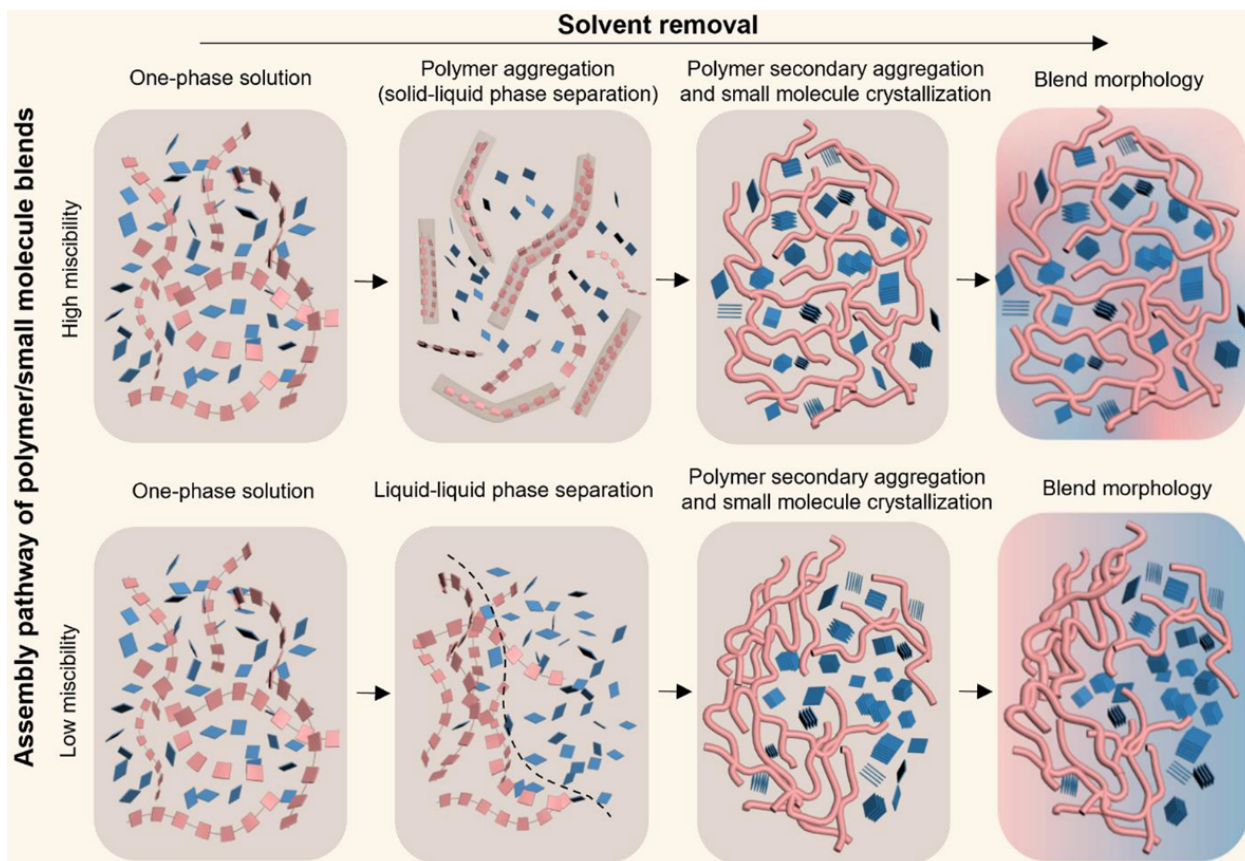


Figure 3. Assembly pathway of polymer/small molecule blends. The initial mixed one-phase solution containing the polymer and small molecule undergoes solid-liquid or liquid-liquid phase separation depending on the miscibility of the materials. Following the phase separation is further aggregation of the polymer and crystallization of the small molecule leading to the distinct phase-separated blend morphologies largely determined by the phase separation and assembly processes. Adapted from [4].

2.3 Stilbene

(E)-Stilbene or commonly known as *trans*-stilbene (hereafter referred to as stilbene) is a molecular organic crystal constituted by aromatic hydrocarbon molecules, $C_{14}H_{12}$ (see **Figure 4**). Stilbene generally is known for its excellent scintillating properties (i.e., light output) making it one of the best organic scintillators—single crystal stilbene incorporation into radiation detectors has proven that it is better suited for fast neutron spectroscopy and neutron-gamma discrimination than any other organic scintillators [7].

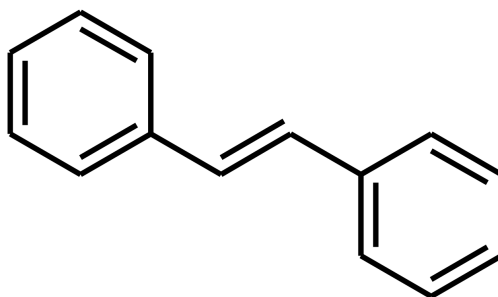


Figure 4. Structural formula of *trans*-stilbene molecule.

3 Studied Samples and Experimental Methods

The following sections describe the preparation of samples containing a polymer/stilbene blend layer. Additionally, several methods for characterizing these layers are briefly presented. While this research focuses primarily on electrical characterization, structural and optical analyses remain critical: they provide essential insight into layer properties and allow for the control of physical and morphological conditions necessary for reliable electrical measurements.

3.1 Sample Structure and Fabrication

The architecture of the fabricated samples is illustrated in **Figure 6**. This structure follows a relatively straightforward design, utilizing a glass substrate onto which a bottom aluminum blocking electrode is deposited. Subsequently, an organic blend layer consisting of a polymer/stilbene matrix is applied. The device is completed by the deposition of a top aluminum blocking contact, resulting in a parallel-plate capacitor geometry. This specific configuration is highly suitable for both core electrical characterization techniques employed in this study: Carrier Extraction by Linearly Increasing Voltage (CELIV) and Time of Flight (TOF).

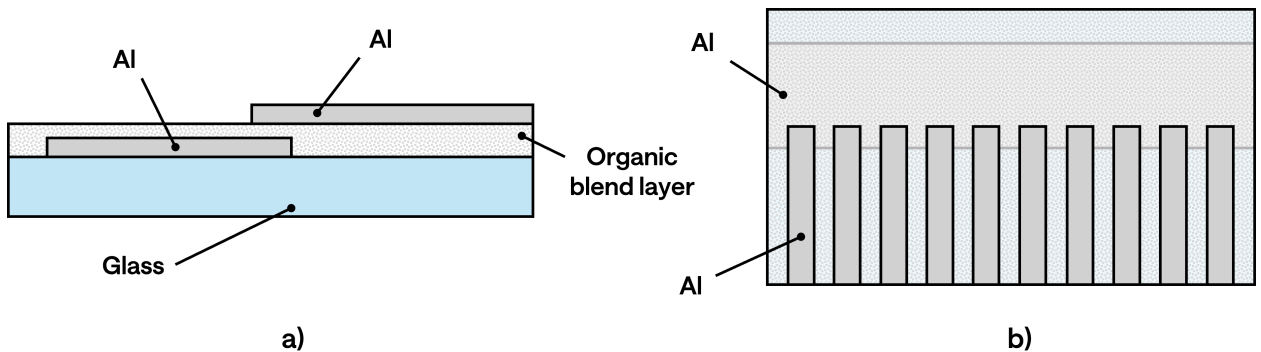


Figure 6. Schematic representation of the sample architecture utilized for the electrical characterization of polymer/stilbene blend layers. (a) Side-view illustrating the vertical layer sequence; (b) Top-view showing the electrode configuration. Total substrate dimensions are 2.5×2.0 cm. Adapted from [16]

The sample fabrication process begins with a cleaning procedure, where the glass substrate is submerged in a series of solvents and treated in an ultrasonic cleaner. Following this, a bottom aluminum contact is deposited via vacuum thermal evaporation. To ensure optimal surface quality, plasma sputtering is subsequently employed for additional debris removal and wetting enhancement. Immediately thereafter, a solution containing stilbene (96% purity, Sigma-Aldrich) and a polymer, dissolved in chloroform, is spin-coated onto the prepared substrate. Once the blend layer has formed, the top aluminum contacts are deposited using the same vacuum thermal evaporation technique; in this step, however, the electrodes are patterned using a shadow mask to define the final geometry.

The prepared samples feature a blend polymer/stilbene layer where ratio of the said materials are adjusted. The **B** series samples utilize a polyvinyl butyral (PVB) polymer as a blend material, while the **P** series samples use poly-N-epoxypropyl-carbazole (PEPC). The summary of investigated samples together with spin-coating parameters is presented in a table below.

Table 1. Summary of the sample configurations investigated in this study. Note that only a couple of the listed samples yielded viable data for electrical characterization (see **Chapter 4** for a detailed analysis).

Name	Stilbene conc. in solution, mg/mL	Polymer conc. in solution, mg/mL	Material ratio	Blend layer thickness, μm	Spin-coating parameters
B1	40	40	1:1	1.61	3000 rpm 750 rpm/s 210 s
B2	80		2:1	3.28	
B3	120		3:1	4.63	
B4	160		4:1	6.20	
P1	40		1:1	1.62	
P2	80		2:1	2.24	
P3	120		3:1	0.15	
P4	160		4:1	0.05	

The above table denotes organic layer thickness calculated from standard CELIV. For the **P** series samples, layer thickness inconsistency can be observed, particularly in P3 and P4 samples (highlighted in red). For this reason, layer thickness is also derived from VASE fit results, and a value of 1.1 μm is accepted for all **P** series samples. For additional information, refer to **Chapter 4.3**.

3.2 Utilized Polymers

Initially, three polymers were evaluated in attempts to achieve an acceptable morphology of the polymer/stilbene blend layer. Polymers PVB and PEPC rapidly demonstrated the desired structural characteristics, therefore the entire fabrication process was subsequently focused exclusively on these two polymers, and the remaining polymer material (polycarbonate (PC)) was no longer considered as potential blend component.

That being said, completely ruling out PC as a polymer blend component may be premature, as polarized light microscopy images of PC/stilbene layer showed decent local crystallinity (see **Figure 33** in **Appendix 1**). Numerous technological parameters (such as solvent choice, concentration, processing conditions, etc.) can still be modified or entirely re-optimized, potentially leading — now or in the future — to equivalent or even superior morphological and material properties.

All three investigated polymers are shown in the **Figure 7** for completeness

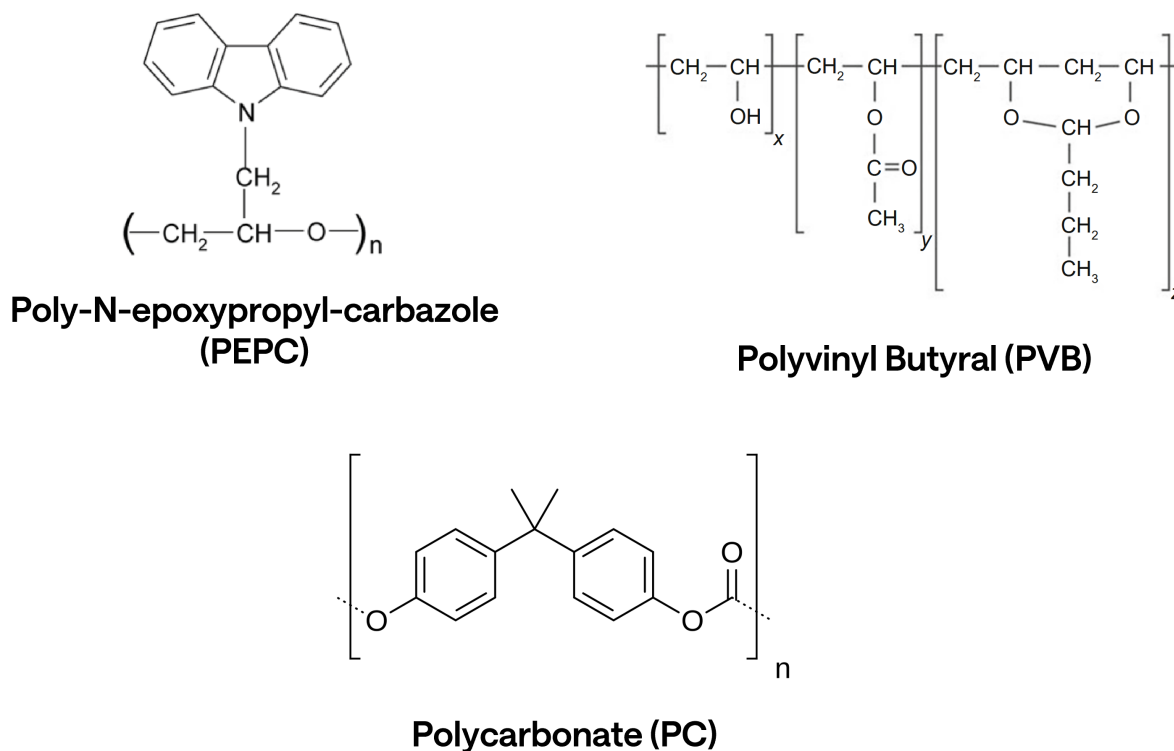


Figure 7. Structural formulas of PEPC (taken from [17]), PVB (taken from [18]) and PC.

3.2.1 Poly-N-epoxypropyl-carbazole (PEPC)

PEPC is a polymer characterized by side carbazolyl groups attached to the main chain. Structurally, it is considered an atactic, amorphous material that shows no evidence of crystallinity, which contributes to its excellent solubility in common organic solvents like tetrahydrofuran and chloroform. PEPC is a well-known organic photoconductor and therefore is extensively used in applications such as electrophotographic microfilming, the manufacture of multicolour slides, and the photothermoplastic recording of information. Regarding its optical properties, PEPC exhibits strong absorption in the near UV spectral region, where it shows photosensitivity up to 345 nm [19–21].

3.2.2 Polyvinyl Butyral (PVB)

Built from three distinct building blocks, the chemical structure of PVB consists of: polyvinyl alcohol (x, 18–23%); polyvinyl acetate (y, less than 1%); and polyvinyl butyral (z, approximately 81%). Typically, the PVB polymer is used in applications requiring strong chemical bonding, optical transparency, and excellent surface adhesion. Furthermore, PVB serves as a blender/binder material [18].

3.3 Structural Characterization

For identifying the polymer/stilbene blend layer crystallinity (particularly crystallite size) and dominant crystallographic planes, structural characterization methods: polarized light microscopy and XRD, were used. The imaging and measurements of samples were performed prior to the top electrode deposition. The utilized techniques are briefly described in the following sections.

3.3.1 Polarized Light Microscopy

Polarized light microscopy examines the molecular order within heterogeneous systems by probing the local anisotropy of a crystal’s optical properties, namely birefringence, which is the anisotropy of the refractive index. In a conventional setup, crossed polarizers (oriented at 90° relative to one another) block light transmission unless the light interacts with a birefringent crystal that modifies its polarization state. By comparison, a parallel configuration permits the entire intensity of polarized light to pass through. Together, these configurations provide quantitative information about how a specimen shifts the phase of light, making them especially useful for identifying crystal domains and mapping molecular orientations [22].

To identify the crystal domains present within the polymer/stilbene blend layer, an OLYMPUS BX41 optical microscope equipped with polarizers was used. The results are presented in **Chapter 4.1**.

3.3.2 X-ray Diffraction

X-ray Diffraction (XRD) relies on the ability of crystalline materials to diffract X-rays in a characteristic way that is governed by their periodic atomic arrangement. The technique is based on Bragg’s Law ($n\lambda = 2d_{hkl} \sin \theta$), which states that constructive interference takes place when X-rays hit crystallographic planes at specific angles (θ) determined by the lattice spacing (d) and the X-ray wavelength (λ). By analyzing the intensity and positions of the diffracted peaks, it becomes possible to determine the orientation of particular lattice planes—identified by Miller indices (hkl)—and to characterize the material’s internal structure and phase composition [23].

The diffraction peaks of the polymer/stilbene blend layers were analyzed using a Rigaku X-ray diffractometer. The predominant crystallographic planes were identified using the SmartLab Studio analysis software database, and the obtained results are presented in **Chapter 4.1**.

3.4 Optical Characterization

Optical techniques such as absorption spectroscopy and Variable Angle Spectroscopic Ellipsometry (VASE) play an essential role in meeting the requirements of electrical characterization methods and in enabling reliable determination of the electrical properties of polymer/stilbene blend layers. Similarly to the structural characterization procedures, the optical measurements were carried out before deposition of the top electrodes onto the samples. The operating principles of the optical characterization techniques are discussed in the following sections.

3.4.1 Absorption Spectroscopy

From the Lambert's law of absorption, which states that the intensity of light decreases exponentially over the distance d of an absorptive medium:

$$I = I_0 e^{-\alpha d} \quad (3)$$

a quantity of absorbance A , can be expressed as:

$$A = \ln \frac{I_0}{I} = -\alpha d \quad (4)$$

which is essentially a Beer-Lambert law for transmittance when scattering is minimal.

By probing the amount of light before and after the sample and plotting the absorbance A (or αd) against wavelength, an absorption spectrum of the material in interest can be acquired.

UV-NIR white light fiber spectrometer from Avantes was used to measure polymer/stilbene blend layer optical absorption spectra. The results are presented in **Chapter 4.2**.

3.4.2 Variable Angle Spectroscopic Ellipsometry

VASE is a non-invasive optical technique, dedicated for characterizing surfaces, interfaces, and thin-films. The analysis of the change in the polarization state of light upon reflection or transmission through a sample, enables identification of essential parameters, such as, thin-film thickness d and optical constants n , k from the ellipsometry measurement. The method extracts information from every layer that interacts with the incoming light beam. The term “ellipsometry” originates from the tendency of polarized light to become elliptical after being reflected [24].

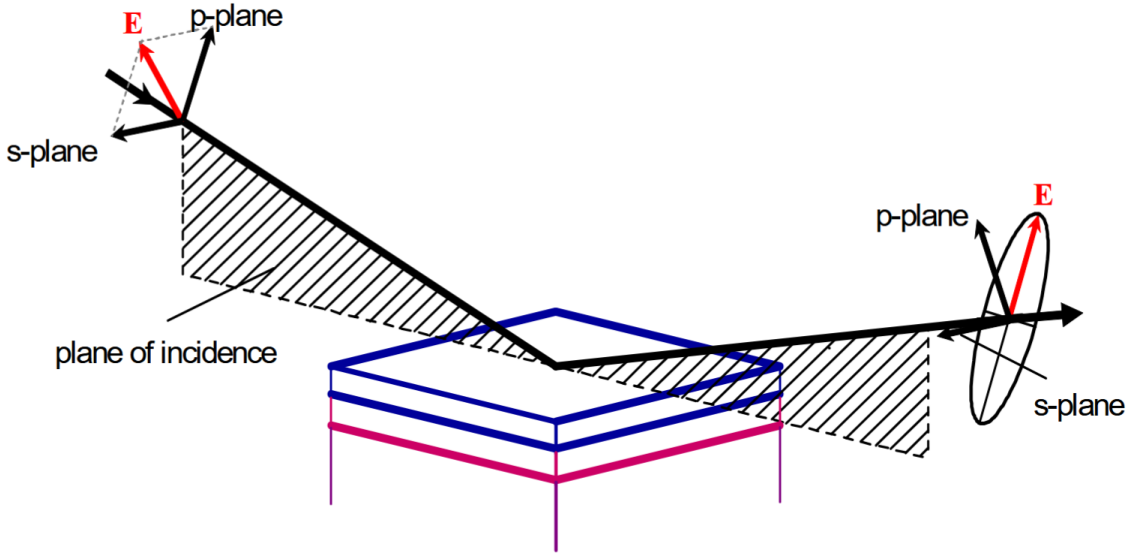


Figure 8. Polarized light interaction with a material. Here, p polarization refers to light polarized parallel to the plane of incidence, while s polarization refers to light polarized perpendicular to it. Taken from [24].

The essential parameters, Δ and Ψ , which are measured in ellipsometry, depend on wavelength and angle of incident, and are expressed as [24]:

$$\tan \psi = \frac{|R^p|}{|R^s|} \quad (5)$$

$$\Delta = \delta_p - \delta_s \quad (6)$$

Ψ represents the angle whose tangent gives the ratio of amplitude attenuation (or magnification) upon reflection for p and s polarizations, while Δ represents the difference between the phase shifts experienced upon reflection by p and s polarizations [24].

The relation between Δ and Ψ parameters is expressed through a complex quantity ρ , which is the complex ratio of the total reflection coefficients [24]:

$$\rho = \tan(\psi)e^{i\Delta} = \frac{\tilde{R}_p}{\tilde{R}_s} \quad (7)$$

Alpha-SE ellipsometer from J.A. Woollam was used for VASE measurements of the polymer/stilbene blend layers, while optical modeling was carried out via CompleteEASE analysis software. Results are presented in **Chapter 4.3**.

3.5 Electrical Characterization

Charge carrier transport and recombination processes in polymer blend layers containing stilbene were investigated using two widely established electrical characterization methods: photo-CELIV and TOF. Detailed descriptions of these techniques are provided in the subsequent subchapters.

3.5.1 Carrier Extraction by Linearly Increasing Voltage

Carrier Extraction by Linearly Increasing Voltage method has many implementations, which suit different materials and different sample geometries. In this study two types of the said method are used: regular CELIV and photo-CELIV.

The regular CELIV is a method used to evaluate drift mobility and bulk conductivity in disordered solids. The principle of CELIV is to apply an increasing voltage pulse to a sample with blocking contact and examine the current transient [25]. Similarly, the same principle applies to photo-CELIV, however, here extraction of photogenerated carriers is examined [26]. Typical transients of both methods are depicted in **Figure 9**.

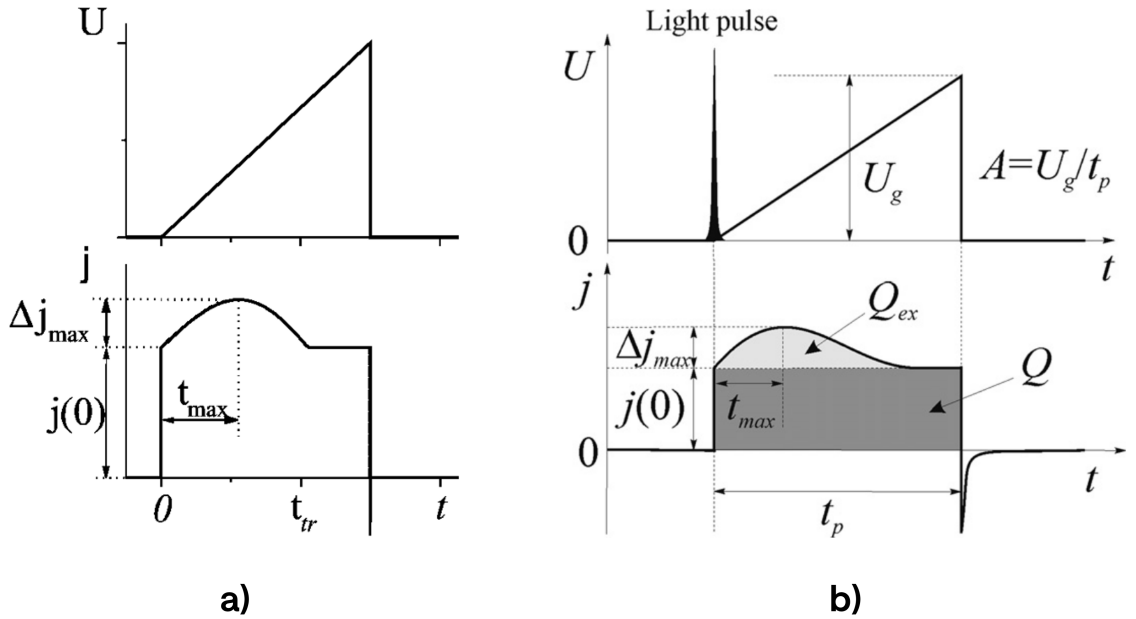


Figure 9. Schematic illustration of applied voltage U to the sample and corresponding current transient j in regular CELIV (a) (adapted from [25]) and in photo-CELIV (b) (adapted from [26]) method. $j(0)$ is the initial current, Δj - extraction current of charge carriers, Q_{ex} - extracted charge, and Q - charge on the electrodes.

In CELIV from the initial voltage step U_0 (scope output — not recalculated to $j(0)$), organic thin-film thickness d can be calculated using [27] (valid when RC is small):

$$d = \frac{\varepsilon \varepsilon_0 S A R}{U_0} \quad (8)$$

where S is overlapping contact area, A is voltage slope and R - load resistance.

As is evident, from both methods, when the extraction is present, charge carrier mobility can be estimated using the t_{max} value, and the mobility expression is:

$$\mu = \frac{2d^2}{3A(t_{max})^2}. \quad (9)$$

However, when employing the photo-CELIV method and establishing a surface photo-generation condition ($\alpha d \gg 1$) the mobility expression changes to:

$$\mu = \frac{2d^2}{A(t_{max})^2}. \quad (10)$$

Both **Equation 9** and **Equation 10** are valid when the photogenerated charge is small compared to the charge accumulated in the contacts.

Another key idea and the main advantage of photo-CELIV is that by varying the delay time t_{delay} between light and voltage pulses, the relaxation of the mobility and the density of charge carriers after photoexcitation could be determined [26].

In the case of analyzing the relaxation of the photogenerated charge carrier density, it is possible to estimate the charge carrier lifetime τ and identify the dominant recombination mechanism in investigated material [28]. To do this, the density of photogenerated charge carriers is first determined by integrating the area under the photocurrent transient and subtracting the capacitive contribution. The resulting charge carrier density values are then plotted as a function of delay time [28].

In some cases, the photocurrent transients measured in photo-CELIV show only partial extraction of charge carriers. When this happens, it is not possible to reliably determine how the charge carrier density relaxes over time. However, if the partial extraction is very close to full extraction (i.e. the transient is nearly ideal), and the main reason preventing complete extraction is the long-lasting tail of the photocurrent transient, and a generally low photoresponse of the material, then there exists a method that still allows a reasonable estimation of the charge carrier density relaxation [16].

The method is based on three key steps:

1. Measuring the main (majority) extracted charge – this corresponds to nearly full extraction of the photogenerated carriers. It is obtained by applying the short-duration CELIV voltage pulse (with pulse length t_p) at a certain delay time after photoexcitation [16].
2. Separately determining the constant "tail" charge – this is the small remaining charge that is extracted very slowly. It is quantified by significantly increasing the CELIV pulse duration t_p until the transient clearly shows full extraction (no more significant tail remains) [16].

- Combining both values – by using the main extracted charge together with the constant tail charge, and then systematically varying the delay time t_{delay} between photoexcitation and the voltage pulse, it becomes possible to reliably evaluate how the charge carrier density relaxes over time [16].

In essence, the approach corrects for the incomplete/short-pulse extraction by accounting for the persistent slow tail, allowing charge carrier density relaxation to be estimated even when perfect full extraction is not achieved with normal short t_p pulses (in low photoresponse materials) [16].

A few important points should be highlighted. Firstly, since extending the duration of the CELIV pulse allows to probe the "tail" charge, one might ask — why not simply use a much longer CELIV pulse to achieve a complete extraction of all charge? The reason is that significantly increasing the CELIV pulse duration usually reduces the amplitude and changes the shape of the photocurrent transient corresponding to the initial (fast) extraction phase. In materials with low photoresponse, this effect becomes particularly problematic: it noticeably increases the error (mainly electrical noise induced) when determining the extracted charge, especially when the delay time (t_{delay}) is varied [16].

Secondly, when determining the main extracted charge as a function of the delay time (t_{delay}), the photocurrent transients recorded for different t_{delay} values must converge to the same final level. This convergence ensures that the shape and magnitude of the slow "tail" part of the photocurrent remain consistent across all delay times — which, in turn, guarantees that the integrated "tail" charge is constant and independent of t_{delay} [16].

The experimental setup used to perform CELIV and photo-CELIV measurements of polymer/stilbene blend samples is illustrated in **Figure 10** and features only a voltage signal generator and an oscilloscope, and a picosecond YAG:Nd laser in the case of photo-CELIV.

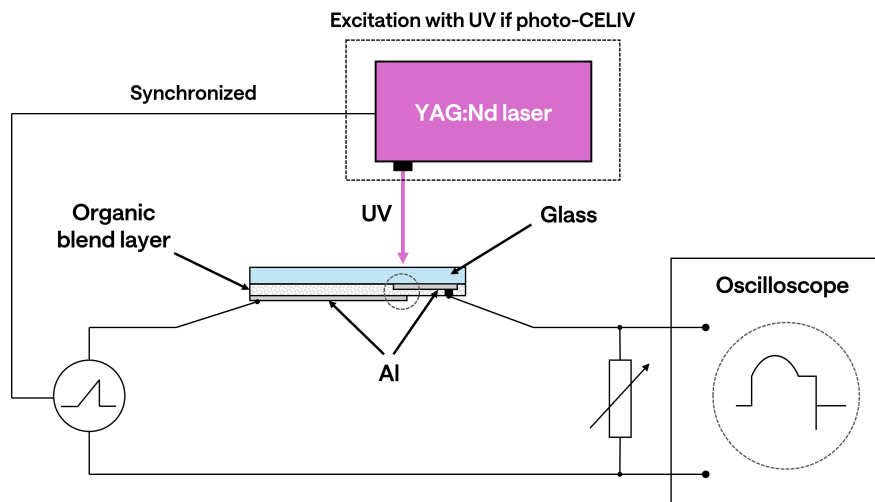


Figure 10. Principal scheme of the CELIV experiment setup. The utilized YAG:Nd laser, in addition to an internal harmonics generator, has a built-in optical parametric amplifier (OPA), which enables the selection of any emission wavelength present in the tuning curves. For photo-CELIV 330 nm and 355 nm wavelengths were used. Adapted from [29].

3.5.2 Time of Flight

Time of Flight is a technique based on measuring the carrier transit time t_{tr} , which is the time required for a sheet of charge carriers photo-generated by pulsed light irradiation at the surface of an electrode to drift across the sample to the other electrode under an applied electric field [30].

To realize a TOF measurement, several conditions have to be satisfied. First, the applied electric field must be uniform and the dielectric relaxation time τ_σ , which is defined as the time for the photogenerated charge to relax back to the original state, should be larger than the t_{tr} . Second, the sample thickness should be significantly larger than the absorption depth, meaning that the light absorption must be at the surface ($\alpha d \gg 1$). Finally, the RC time constant should be much smaller than t_{tr} — differential TOF regime [31].

Typical TOF transients are illustrated in **Figure 11**. The inset in **Figure 11b** shows a standard practice of utilizing double logarithmic scale to easily determine the transit time t_{tr} in dispersive organic materials. The mobility is calculated by **Equation 11**.

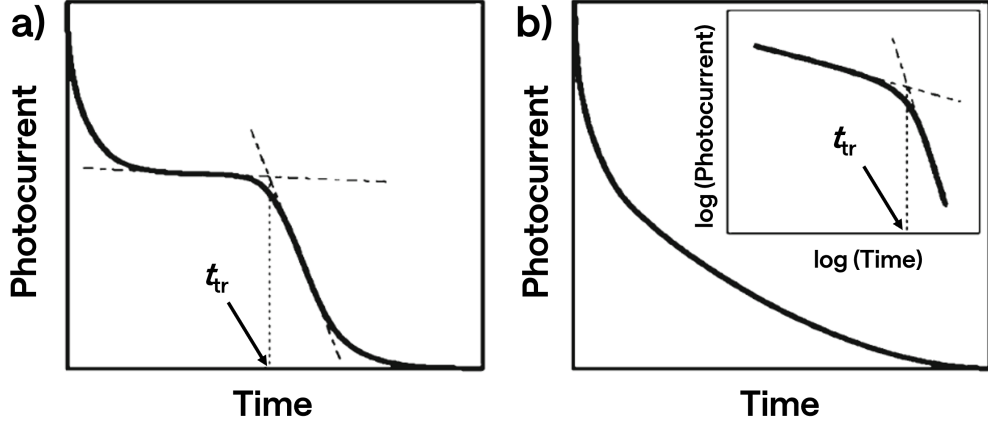


Figure 11. Typical TOF transient photocurrents. (a) Non-dispersive, (b) dispersive. Adapted from [30].

$$\mu = \frac{d^2}{V t_{tr}}. \quad (11)$$

Experimental setup used to perform TOF measurements on the polymer/stilbene blend samples in this study utilizes the same equipment as in the photo-CELIV experiment, however, instead of the signal generator a DC power supply is used as a voltage source. The figure below shows a detailed TOF setup.

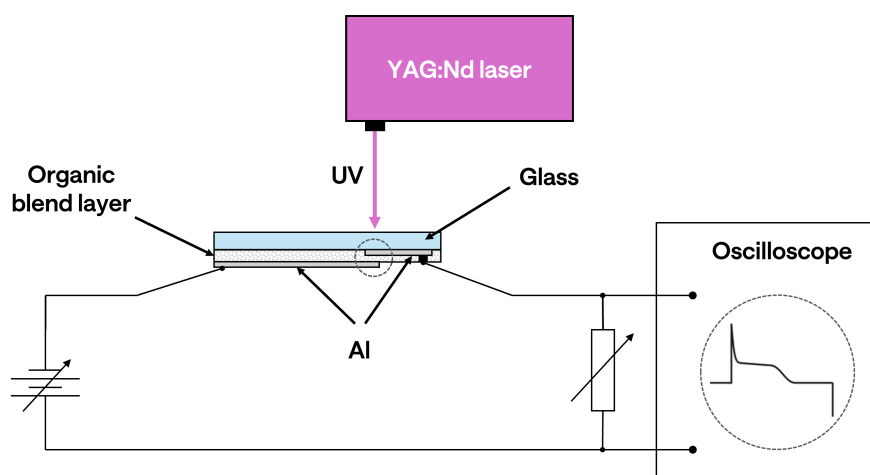


Figure 12. Principal scheme of the TOF experiment setup. The utilized YAG:Nd laser, in addition to an internal harmonics generator, has a built-in OPA, which enables the selection of any emission wavelength present in the tuning curves. For TOF 330 nm wavelength was used. Adapted from [29].

4 Results and Discussion

Polymer and stilbene organic blend layers, utilizing PVB or PEPC as a polymer component, were characterized using techniques described in the previous chapter. The thickness of each fabricated sample (see **Table 1**) was evaluated using regular CELIV measurement and **Equation 8**. Dielectric constant ε value of 3.5 was used in calculations.

4.1 Crystallinity of Organic Layers with Stilbene Crystallites

The polarized light microscopy images of organic layers with PVB polymer and stilbene crystallites (**B** sample series) are presented in **Figure 13**, while images of organic layers where polymer component is PEPC (**P** sample series) are presented in **Figure 14**. The polarizers configurations — crossed and parallel — in images are represented with $\times$ and $=$ symbols accordingly. The stilbene and polymer ratio used during fabrication of the samples is denoted in each row of the images.

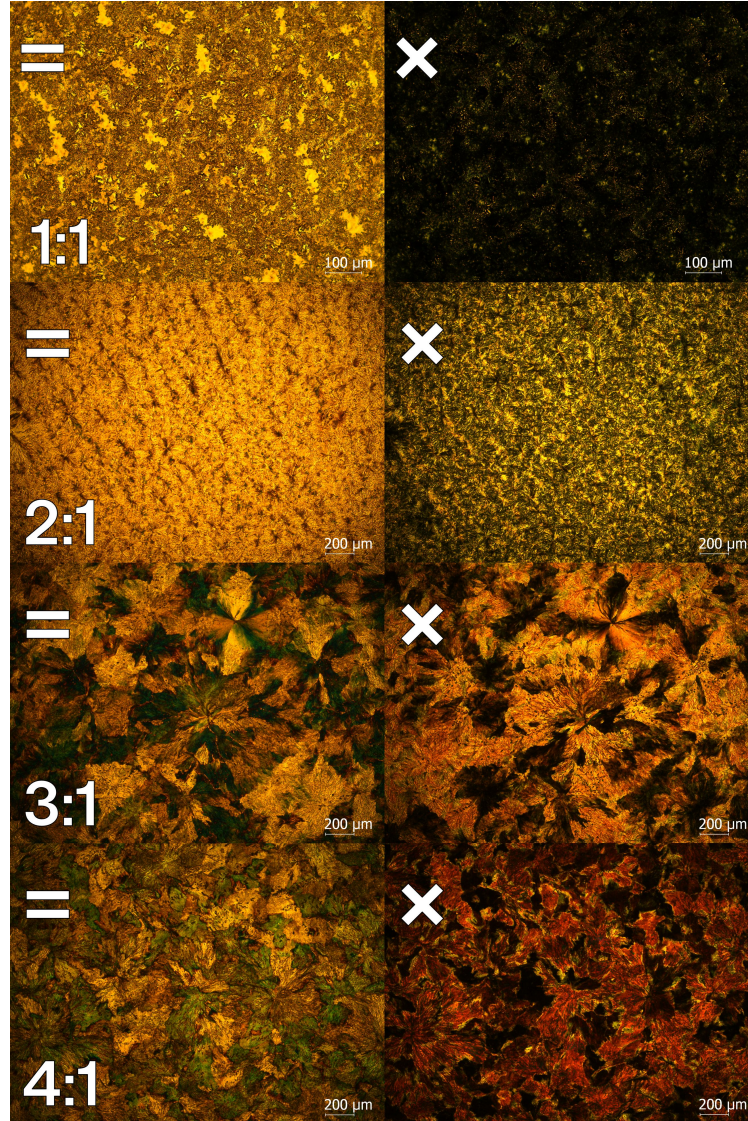


Figure 13. Polarized light microscopy images of organic layers with PVB polymer and stilbene crystallites.

When observing stilbene crystallinity in organic layers of the **B** series samples, it is evident that with increasing amount of stilbene used in layer fabrication, greater crystallinity (or higher abundance of crystal domains) of the layer is noticed. The images of B1 sample suggest perhaps a sparse distribution of relatively small in size stilbene crystallites, or no meaningful crystallinity at all. The B2 sample presents completely opposite layer morphology, as the crystallinity of stilbene has significantly increased. The B3 and B4 sample layers, in addition to increased abundance of crystalline stilbene regions, begin to show (at a surface level) crystal domains positioned at several different directions. Furthermore, the latter two samples in terms of blend layer morphology are very similar.

Even though higher stilbene and PVB ratio samples show favorable degree of stilbene crystalline region abundance, the evaluation of crystallite sizes in these samples is infeasible due to crystal boundary ambiguity.

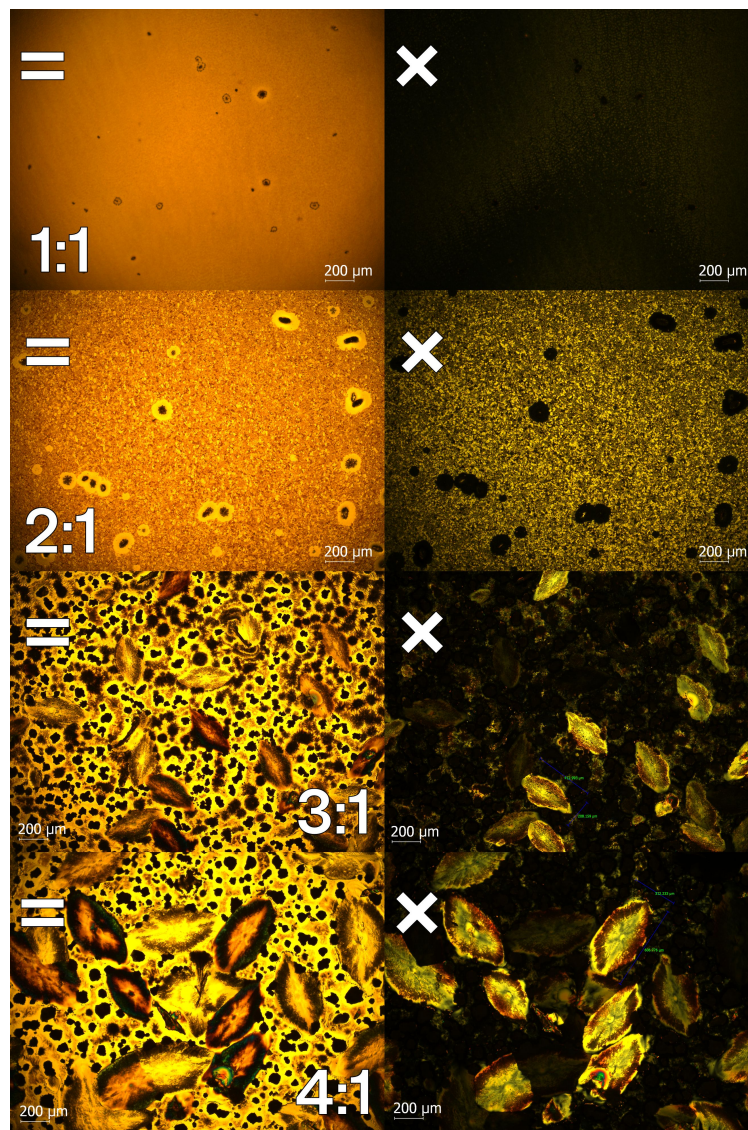


Figure 14. Polarized light microscopy images of organic layers with PEPC polymer and stilbene crystallites.

Similar observations in terms of layer crystallinity can be stated for **P** series samples presented in the figure above. The P1 and P2 sample layer morphologies are highly comparable to the ones observed in B1 and B2 samples. However, key differences between used polymers for layer formation are seen when comparing higher ratio samples. In P3 and P4 layers, contrary to B3 and B4, individual crystallites can be distinguished, and thus their dimensions can be extracted: $\sim 400 \times 200 \text{ }\mu\text{m}$ for P3 and $\sim 600 \times 300 \text{ }\mu\text{m}$ for P4. From this an important observation can be stated, that during P4 sample layer formation (and with presence of higher amount of stilbene in solution), the growth of proportionally larger crystallites was allowed. To add, both P3 and P4 samples show evenly dispersed crystallites throughout the whole layer, thus establishing moderately high degree of crystallinity.

Moving onward, X-ray diffractograms of **B** and **P** series blend layer samples are presented in **Figure 15** and **Figure 16**, respectively. To improve the visual comparison of similarities, the plots are displayed with an applied offset. Note that in several instances throughout both sample series, visible XRD peaks were not assigned to any crystallographic plane, as the analysis software determined the peaks did not originate from stilbene (likely originated from contact material).

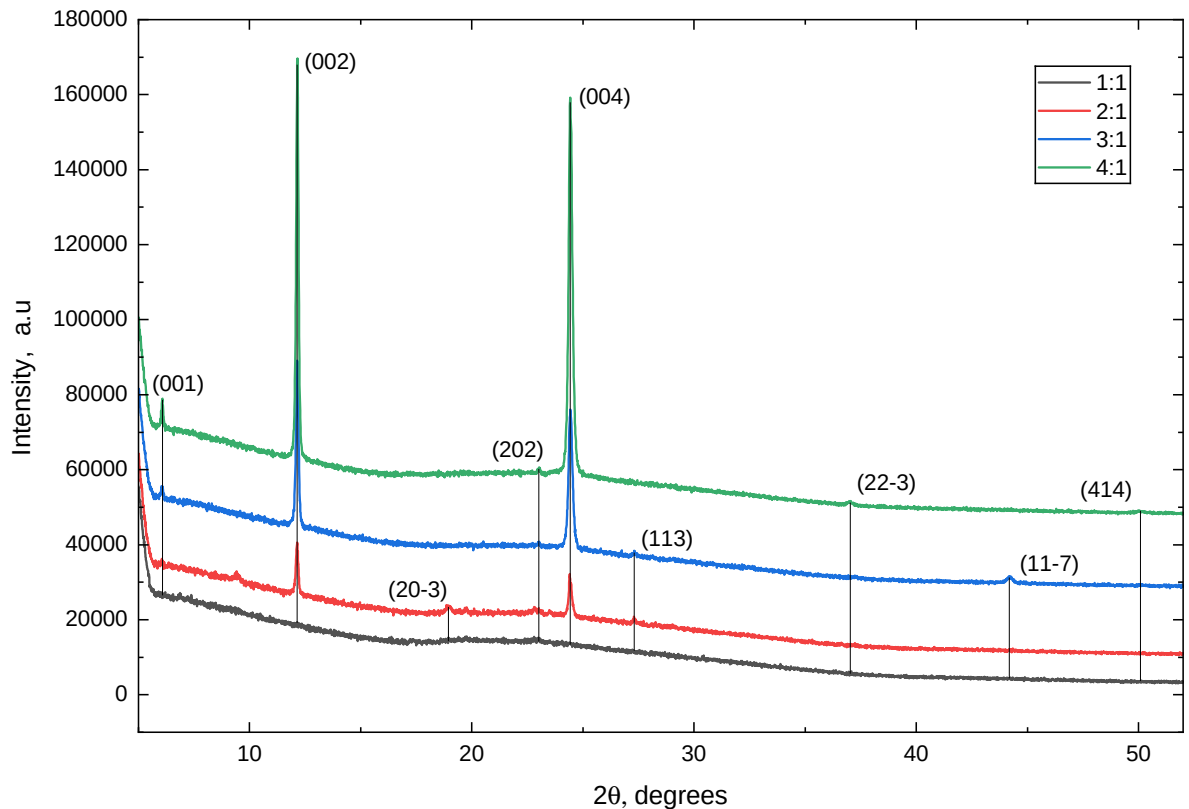


Figure 15. X-ray diffractograms of 1:1, 2:1, 3:1 and 4:1 stilbene and PVB ratio blend samples.

For **B** series samples, it becomes immediately evident, that the highest intensity XRD peaks at 2θ angles 6.128° , 12.139° , 24.408° corresponding to crystallographic planes (001), (002), (004) appear in samples with material ratio 2:1, 3:1 and 4:1, and are absent in the

sample with material ratio 1:1, which in fact does not show any XRD peaks. Comparison with the polarized light microscopy image of the same sample further confirms that stilbene crystallization is strongly suppressed in this case. Furthermore, the 1:1 ratio blend sample exhibits a predominantly amorphous character, evidenced by the more pronounced hump at around $2\theta = 20 - 25^\circ$, which indicates the dominance of the polymer phase.

Very similar findings from X-ray diffractograms of **P** series samples (compared to the **B** series) can be stated: predominant (002) and (004) crystallographic planes for P3 and P4 samples, and polymer phase occurrence in P1 and P2 samples. Some differences, however, can also be observed. Low stilbene/PEPC ratio samples (P1, P2) show the appearance of diffraction peaks attributed to crystallographic planes (20-2), (110), and (111), indicating that, in these samples, the formation of differently oriented crystals is preferred compared to P3 and P4 samples. In all fairness, organic layers from both series show at least small distribution of differently oriented crystals.

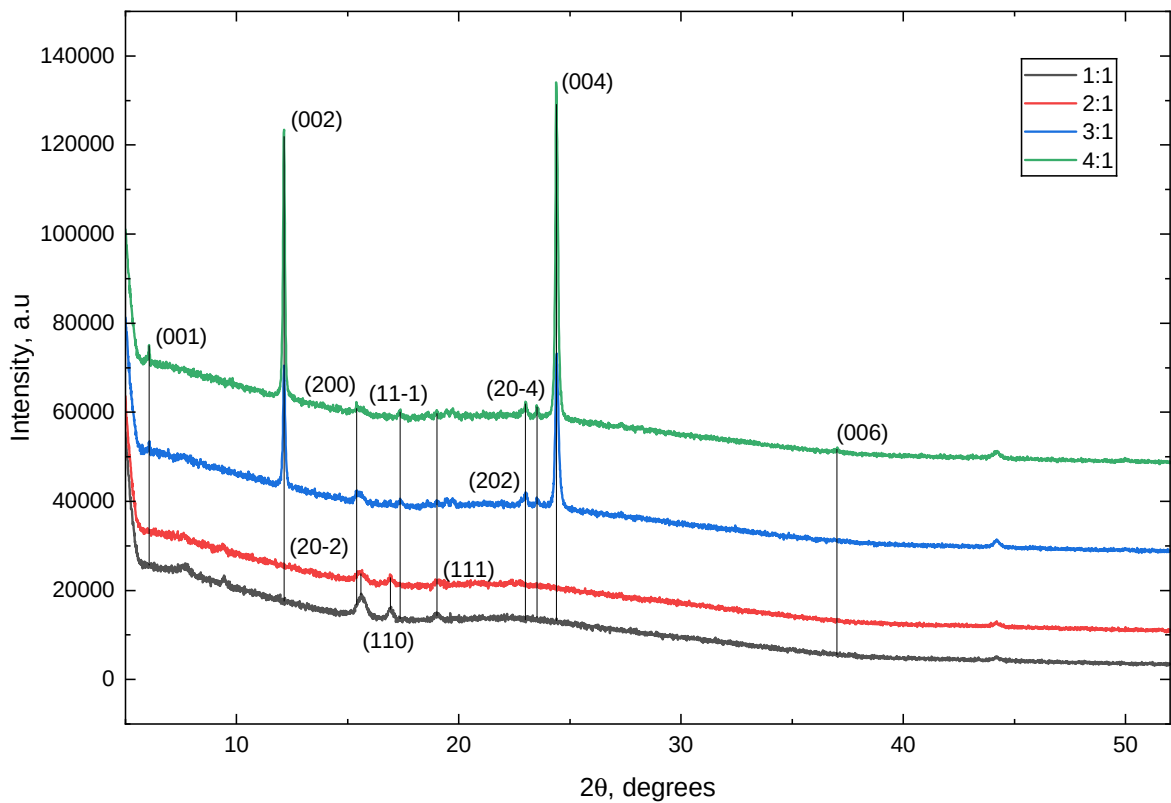


Figure 16. X-ray diffractograms of 1:1, 2:1, 3:1 and 4:1 stilbene and PEPC ratio blend samples.

The predominant stilbene diffraction peaks in organic layers of **B** and **P** series samples (mainly B2–B4 and P3, P4) belong to the same family, are perfectly parallel, and share the same crystallographic orientation. It is therefore reasonable to conclude that the stilbene crystals are well aligned relative to the substrate.

4.2 Absorption Spectra of Organic Layers with Stilbene Crystallites

The absorption spectra of organic layers containing PVB polymer and stilbene crystallites are shown in **Figure 17**, whereas the spectra of organic layers based on PEPC polymer and stilbene blends are presented in **Figure 18**.

The optical absorption spectra measured for the polymer/stilbene blend layers mainly provide insight into the appropriate laser wavelength required for photogeneration of charge carriers, as well as whether carrier generation takes place predominantly at the surface or in the bulk of the material.

The absorption peaks obtained for the **B** and **P** series samples indicate that multiple irradiation wavelengths are suitable for use in photo-CELIV and TOF measurements. Consequently, the selected laser wavelength should correspond to the strongest observed photoresponse.

Moreover, in organic layers of the **B** and **P** series samples with higher stilbene and polymer ratios, the αd parameter is significantly greater than 1, implying that charge carrier generation is expected to occur predominantly near the film surface.

Lastly, from the αd product, thin-film thickness could be extracted, however, due to significant scattering losses ("absorption" increase in visible wavelength range) in polymer/stilbene layers, the evaluated values would be deemed unreliable.

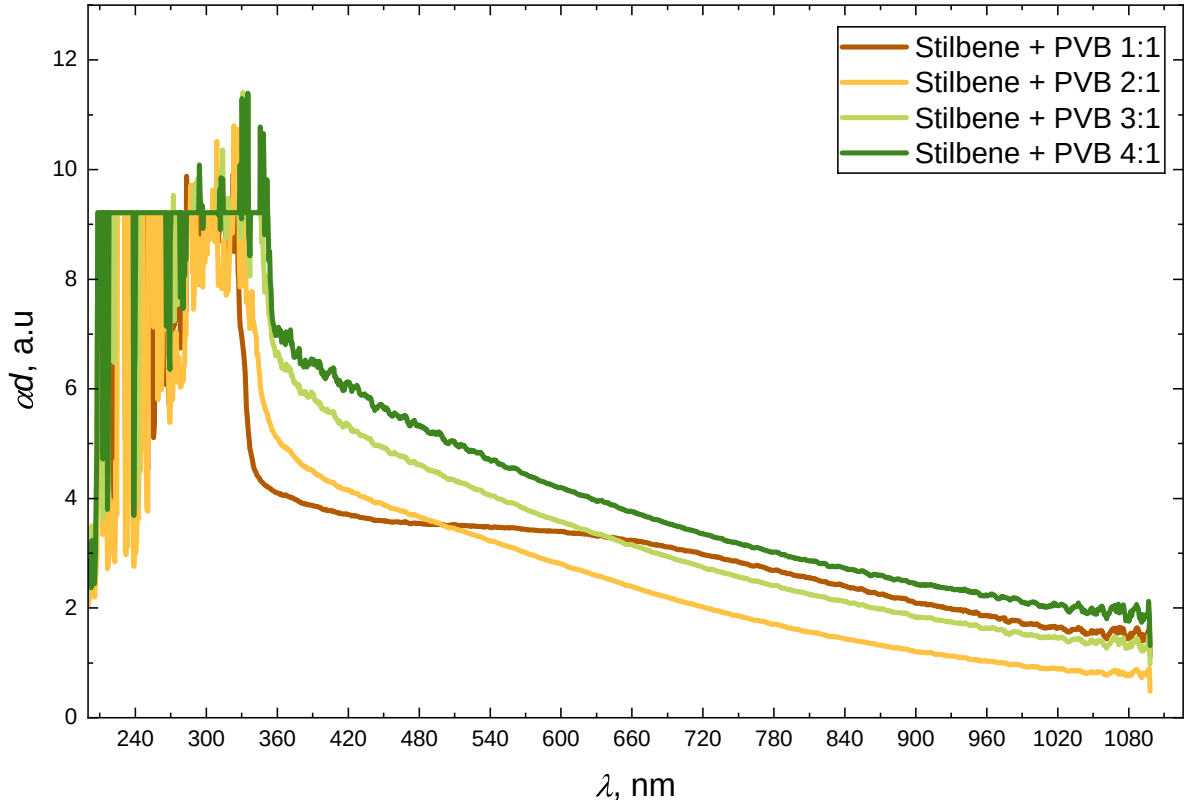


Figure 17. Absorption spectra of investigated PVB/stilbene organic blend layers. Note that the electrical noise in the UV area is left on purpose to show the additional effects of light scattering by the samples. For clarity purposes noise-free spectra is displayed in the previous work [16].

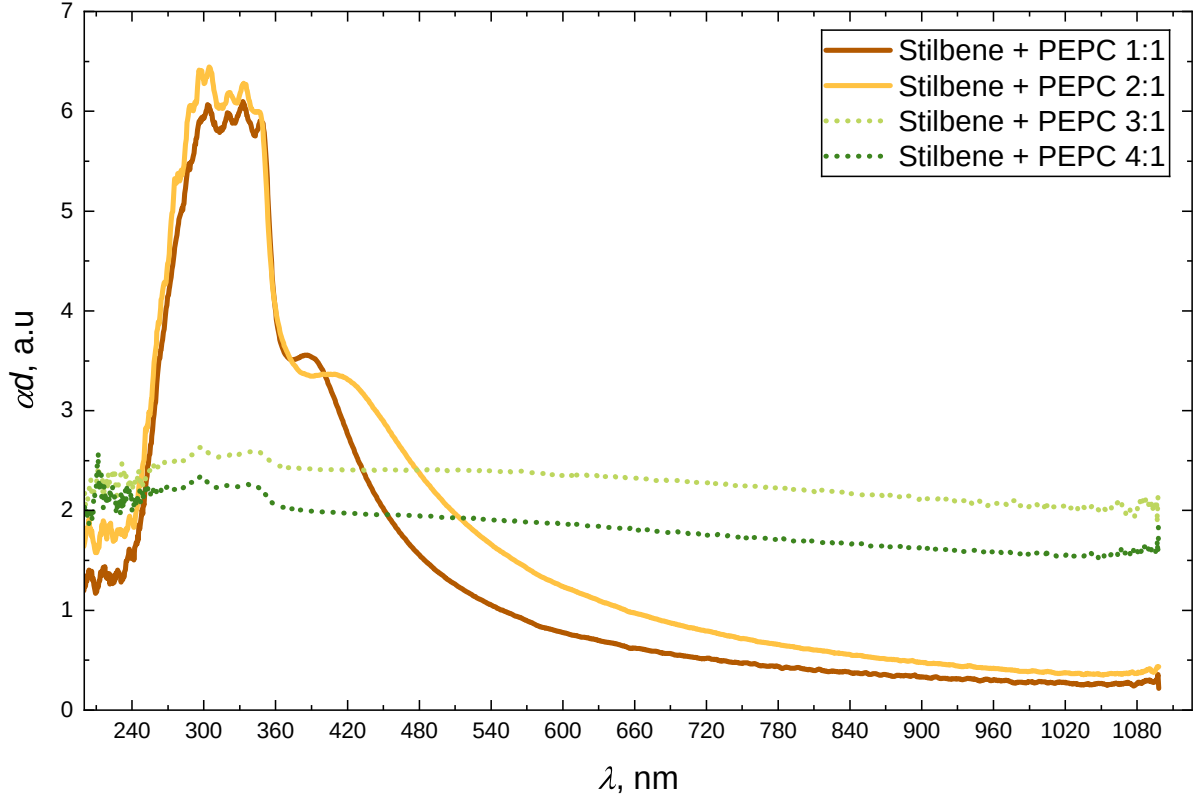


Figure 18. Absorption spectra of investigated PEPC/stilbene organic blend layers. An apparent "disappearance of the absorption" for 3:1 and 4:1 stilbene and PEPC ratio samples can be attributed to the layer morphology (see **Figure 34** in **Appendix 1**), where significant amount of transparent polymer regions during the measurement contributed to transmittance.

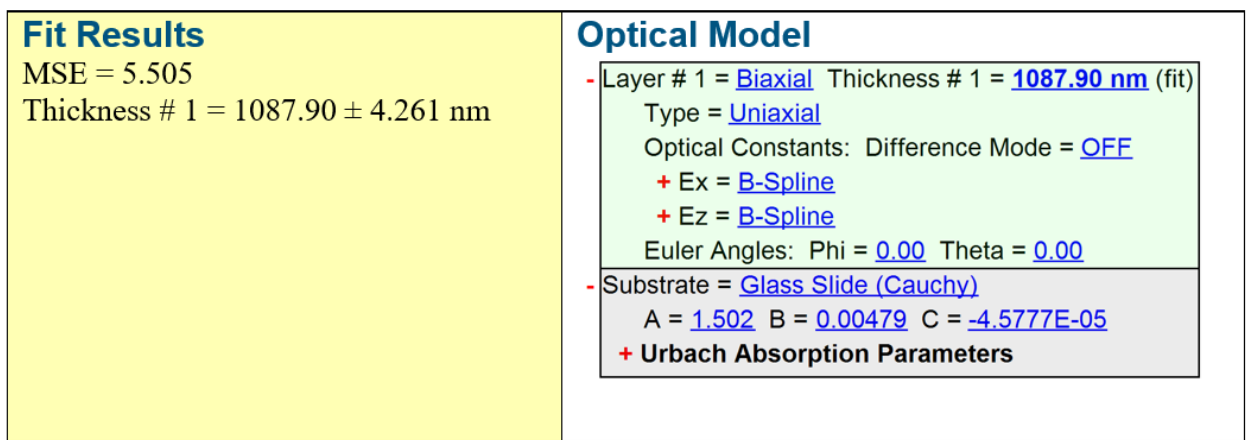
4.3 Evaluation of PEPC/Stilbene Blend Layer Ellipsometry Data

Due to the significant overlap of stilbene crystallites with both the bottom and top electrodes, as well as their high abundance, the evaluation of P3 and P4 sample layer thicknesses using standard CELIV measurements becomes unreliable. Good stilbene and contact arrangement with the high abundance of crystallites, results in a much larger capacitive CELIV signal, making the use of a dielectric constant $\varepsilon = 3.5$, which would correspond to much thinner layers on the order of tens to hundreds of nanometers, inappropriate. Consequently, a higher, stilbene-induced effective ε value should be considered when estimating layer thickness. However, determining the appropriate ε value would require a dedicated study in itself. Therefore, VASE becomes a key tool for estimating these layer thicknesses (provided that the measurements yield sufficiently noise-free data), as the dielectric constant of stilbene at optical frequencies [32] is comparable to typical ε values of organic polymers (3–3.5).

VASE was performed for all **P** series samples, however, only P1 sample yielded noise-free data, which could be modeled for thickness only, omitting the modeling of n , k optical constants. The ellipsometry data fit results are presented in **Figure 19**, and estimate P1 layer thickness equal to $\sim 1.1 \mu\text{m}$.

Given the low viscosity of the stilbene/PEPC solutions (as confirmed by visual comparison) used for depositing the organic layers in the **P** series samples, and considering that the majority of the applied solution is removed from the substrate during spin coating, it can be concluded that the thicknesses of the **P** series samples are approximately the same.

A note should be made regarding the discrepancy between the ellipsometry-estimated thickness of the P1 sample and the value obtained from CELIV, with the latter being $\sim 50\%$ larger. Both values are, however, expected to be correct; therefore, the mobility values obtained for the P4 sample using the TOF technique are compared while accounting for different thickness assumptions. In addition, since the CELIV-calculated thicknesses from P1 to P2 show increase, the thickness for the P4 sample is accordingly extrapolated, yielding a value of $\sim 3.4 \mu\text{m}$.



Experimental and Model Generated Data Fits

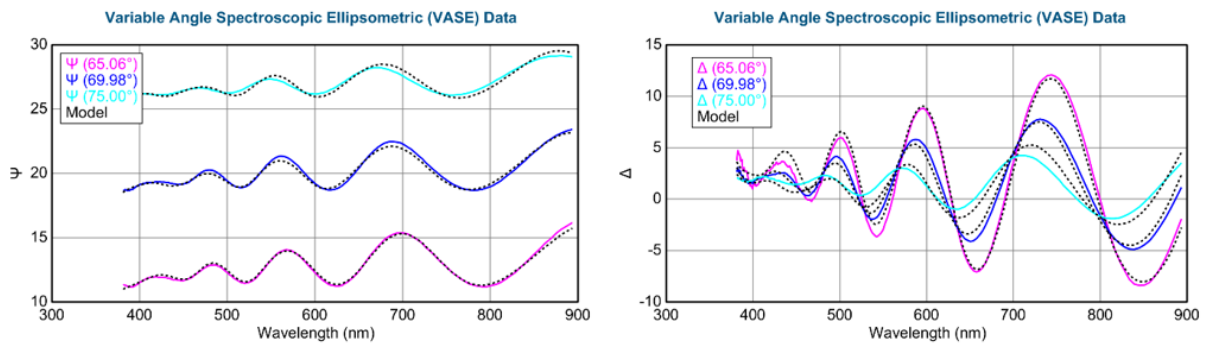


Figure 19. Report of ellipsometry data fit results for P1 sample. Low Mean squared error (MSE) value and a near identical model fit data suggest good thickness estimation.

4.4 Carrier Transport in PEPC/Stilbene Blend Layers

TOF measurements were carried out on organic layers containing PEPC and stilbene crystallites (**P** sample series). However, among all investigated samples, only the P4 sample exhibited a clearly observable transit time in the photocurrent transients. Moreover, it was possible to measure both electron and hole transit times t_{tr} in the organic blend layer. Hole and electron photocurrent transients are displayed in **Figure 20** and **Figure 21**, respectively. Arrows in the graphs point to a transit time t_{tr} value, and a double-logarithmic scale is used to improve the accuracy of its determination. Charge carrier mobility values were calculated using **Equation 11** and are presented as a function of $\sqrt{E}$ in a semi-logarithmic plot (see **Figure 22**). As was mentioned, previously two distinct calculations were performed in accordance to the layer thickness discrepancy.

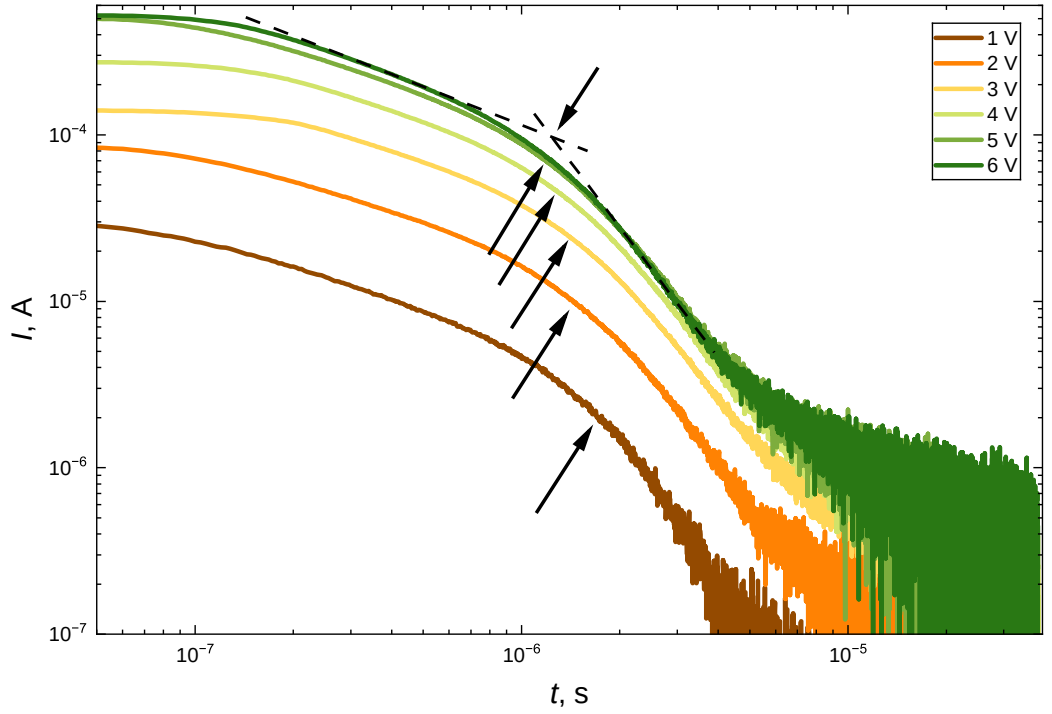


Figure 20. TOF hole photocurrent transients of P4 sample irradiated with 330 nm wavelength laser pulses.

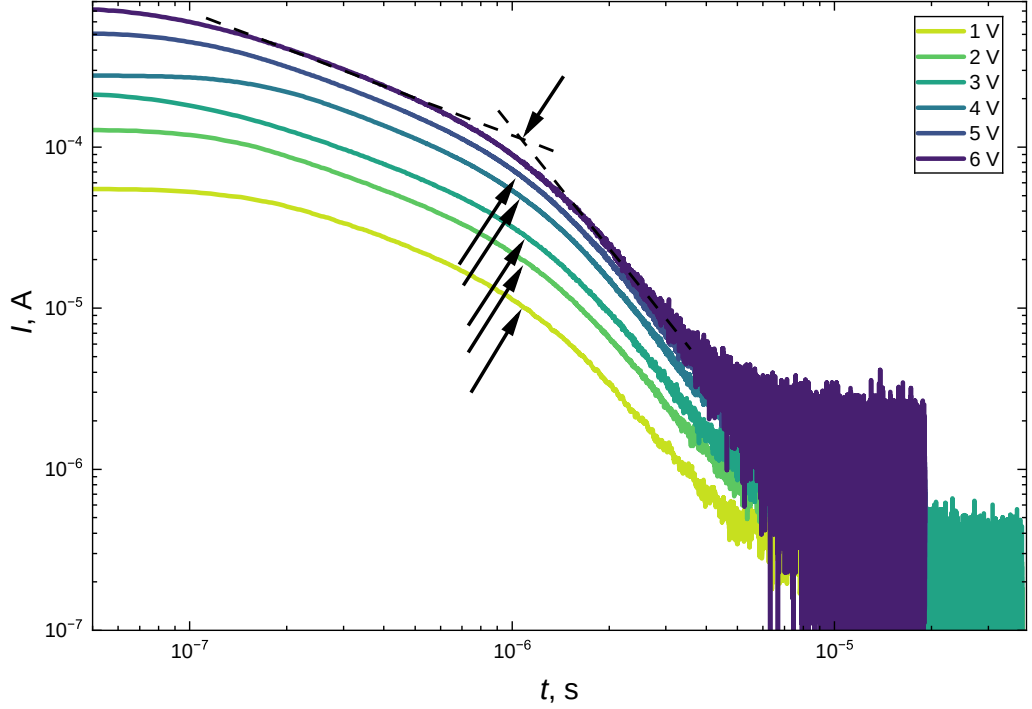


Figure 21. TOF electron photocurrent transients of P4 sample irradiated with 330 nm wavelength laser pulses.

From **Figure 22**, it is apparent that using the extrapolated CELIV sample thickness would yield approximately an order of magnitude higher μ_h and μ_e values compared to the values calculated with ellipsometry-estimated sample thickness, even though the thickness values differed ~ 3 times. Taking into the consideration: the mobility value discrepancy and a low viscosity PEPC/stilbene solution condition used when forming the P4 sample layer, the correct mobility values are accepted to be the ones calculated using the ellipsometry-estimated sample thickness.

The μ_h and μ_e values, thus, fall into the range of $0.001\text{--}0.01\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The difference between μ_h and μ_e values (μ_e value is slightly higher) is slight and at higher electric field value becomes negligible. When talking about the mobility-electric field dependence, the charge carrier mobilities in P4 sample layer decrease with increasing field. The observed result is the opposite of the typical behavior seen in organic materials — increase in applied electric field increases the mobility (Poole-Frenkel law). Such a dependence of decreasing mobility is typically observed at low electric fields, which corresponds to the conditions of the P4 sample measurements, and can be explained by the Bäessler's Gaussian disorder formalism — at low electric fields charge carriers tend to hop into deep trap states (energetically favorable tail states) and as the electric field increases, the carriers are forced to hop along the field direction, limiting their access to deeper low-energy states and confining transport to higher-energy, less energetically favorable sites. In addition, a possibility of disperse TOF transients, which increases the error in t_{tr} evaluation, must not be forgotten.

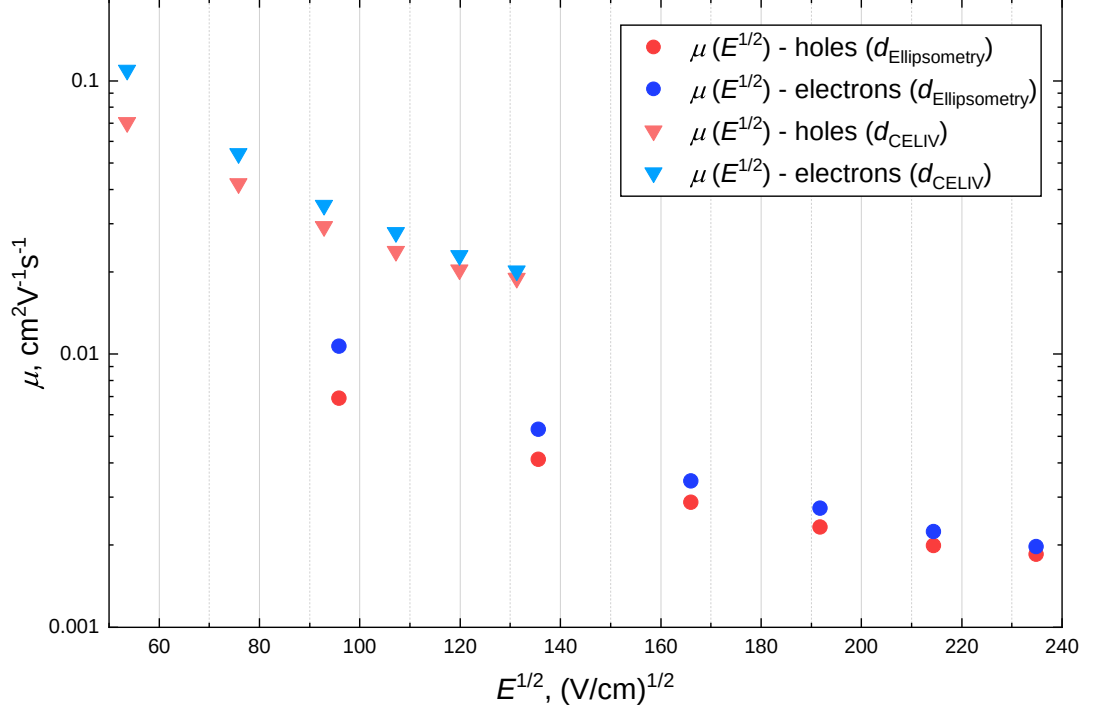


Figure 22. Hole and Electron mobility dependence on electric field in P4 sample.

When comparing hole and electron mobility in the organic layer containing PEPC and stilbene crystallites with literature values reported for single crystals [10, 11], a reduction of about three orders of magnitude for holes and two orders of magnitude for electrons is observed. This clearly indicates hindered charge transport in such a blend-layer morphology. Although structural and energetic disorder reduces the inherently high mobility of pure stilbene in this configuration, the resulting mobility is still relatively high in the context of organic materials, and the observed morphology suggests promising potential for applications in organic electronic devices.

4.5 Carrier Transport and Recombination in PVB/Stilbene Blend Layers

Photo-CELIV measurements were performed to organic blend layers containing PVB and stilbene (**B** sample series). However, out of all investigated samples, only the B4 sample produced well-defined photocurrent transients that allowed reliable extraction of charge carrier mobility and photogenerated charge values. Additionally, both hole and electron transport were investigated, and the relaxation of charge carrier density and mobility was determined.

Before presenting obtained results from photo-CELIV measurements and discussing the charge carrier transport and recombination, several important points must be stated about the sample thickness validity. First and foremost, the solutions used for the fabrication of PVB/stilbene blend layers exhibited high viscosity, and during spin coating, nearly the entire volume of solution deposited onto the substrate remained on its surface. Consequently, the thickness values estimated by standard CELIV measurements for the **B** series samples are considered reliable. VASE measurements were additionally carried out in an attempt to verify the CELIV-estimated thicknesses; however, the obtained ellipsometry data were extremely noisy, or, in some cases, measurements could not be performed at all. Due to the strong scattering nature of the samples, the detector was unable to register reflected polarized light from the sample surface.

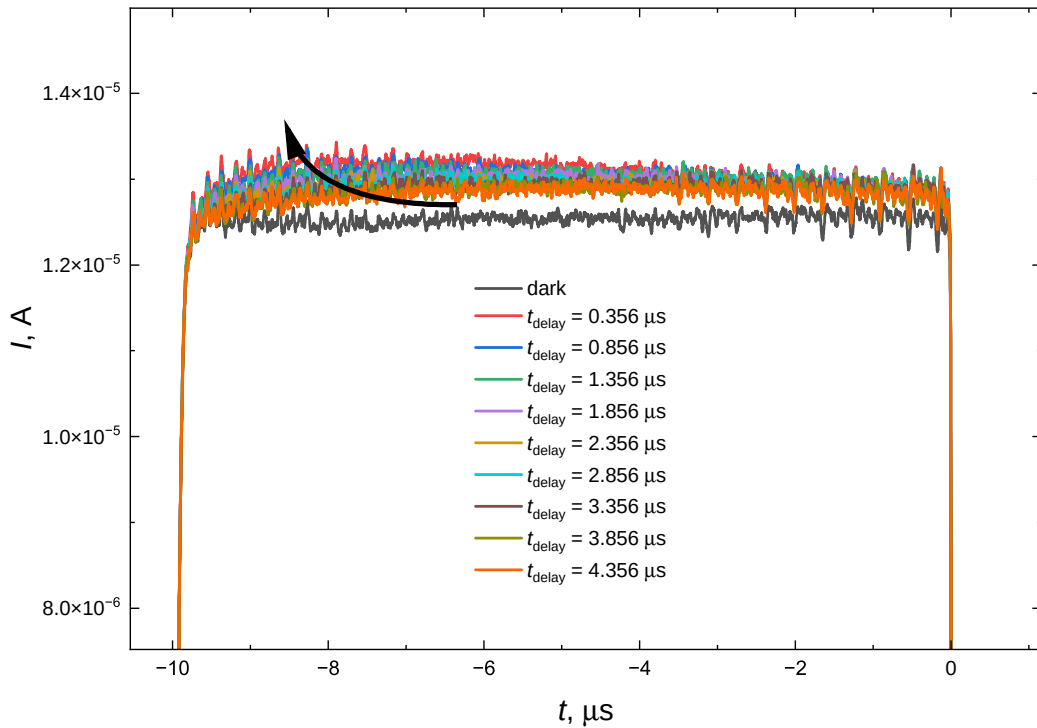


Figure 23. Photo-CELIV current transients of B4 sample. Transients show partial charge carrier extraction. The sample was irradiated with 330 nm wavelength laser pulses. The view is zoomed in.

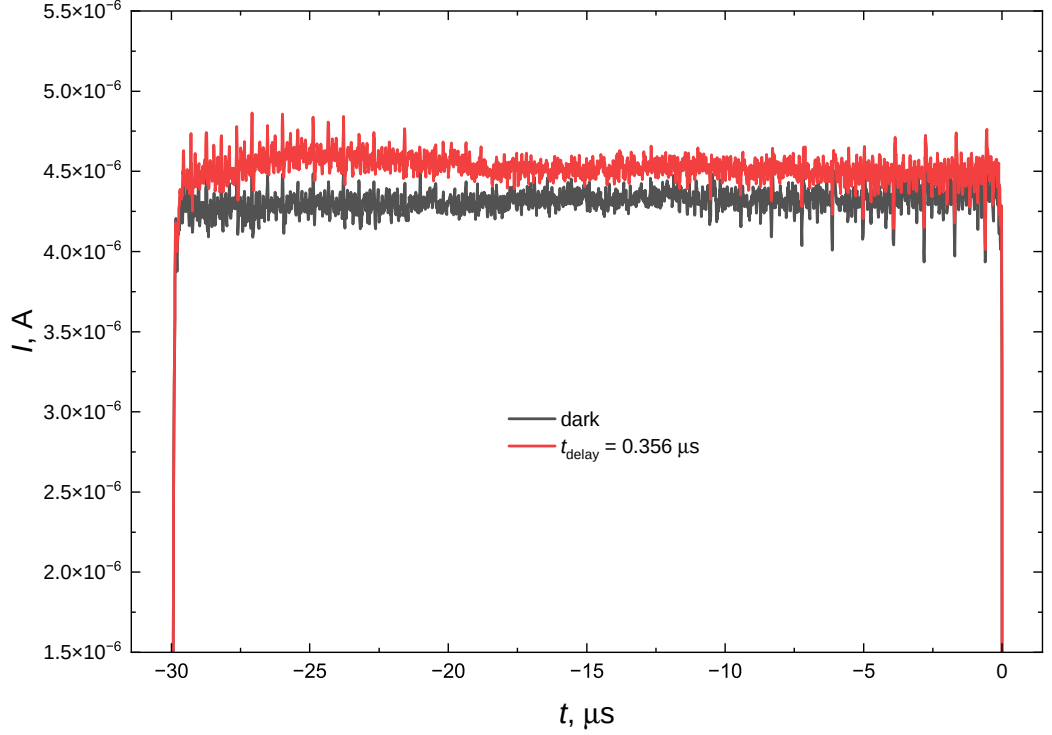


Figure 24. Photo-CELIV current transient of B4 sample. Transient shows full charge carrier extraction. The sample was irradiated with 330 nm wavelength laser pulses. The view is zoomed in.

Initially, the B4 sample was investigated by photo-CELIV using laser pulses with a wavelength of 330 nm, and a novel CELIV approach was applied to determine hole carrier lifetimes. Subsequently, the sample was measured using a different excitation wavelength of 355 nm, which generated a stronger photoresponse, enabled complete charge extraction, and allowed estimation of electron mobility and lifetime. The hole and electron mobility values were calculated using **Equation 10**.

The hole photo-CELIV transients obtained during the first measurement are shown in **Figure 23**. From the extracted t_{max} values, the hole mobility μ_h was calculated and found to lie within the range of $0.01\text{--}0.1\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The dependence of hole mobility on $t_{delay} + t_{max}$ is presented in **Figure 25**. An exponential decrease in hole mobility with increasing delay time is observed, indicating the presence of a single characteristic carrier relaxation time related to energetic relaxation within the disordered density of states rather than intrinsic transport properties.

By combining the majority carrier charge obtained from **Figure 23** with the tail charge extracted from **Figure 24**, recalculating these values to hole density, and plotting the result as a function of $t_{delay} + t_{max}$, the hole lifetime τ_h in the B4 sample can be determined. The corresponding results are presented in **Figure 26**. The observed dependence indicates a monomolecular recombination process, with the estimated hole lifetime being approximately 16 μs .

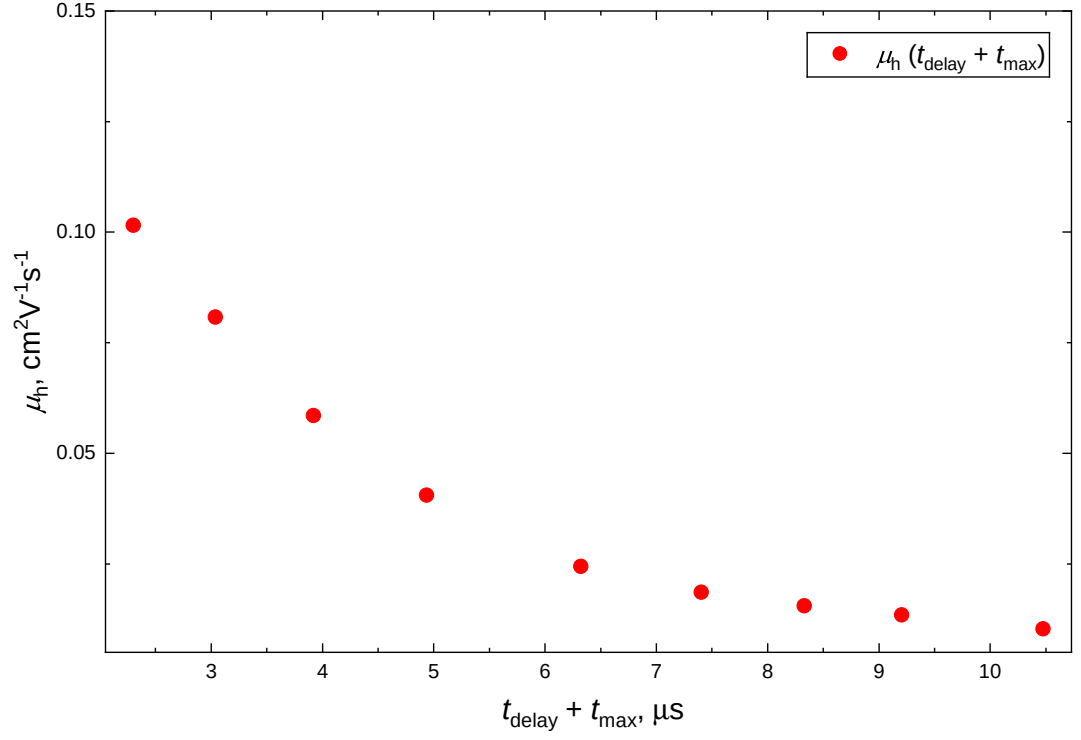


Figure 25. Relaxation of hole mobility determined from photo-CELIV measurements of B4 sample.

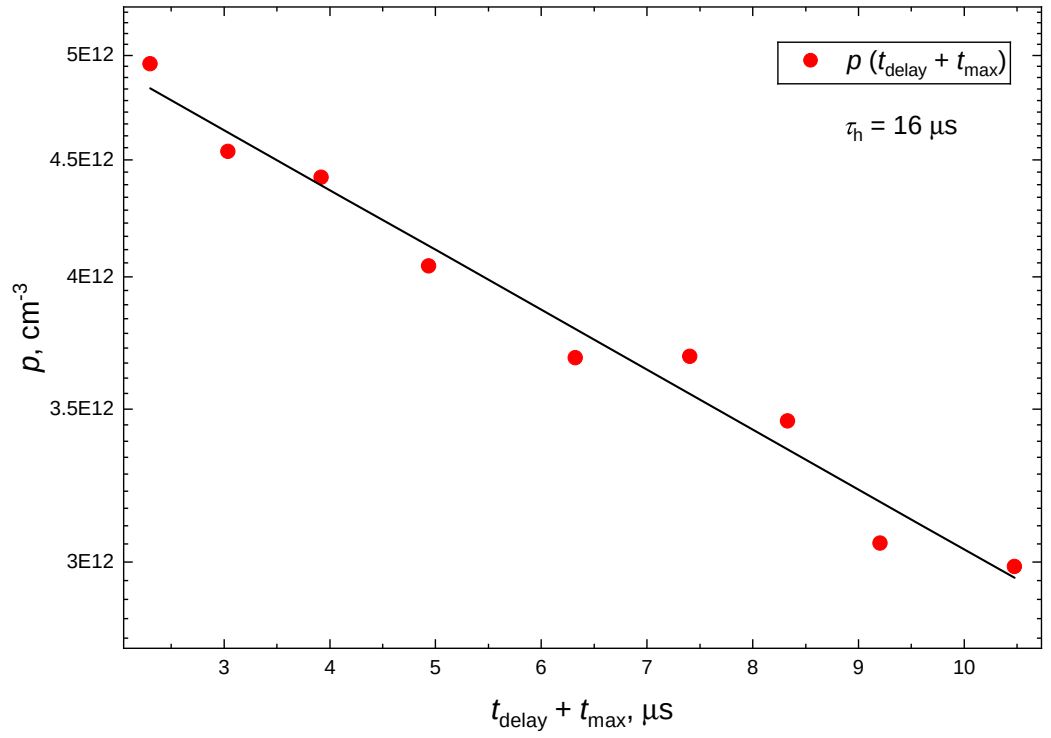


Figure 26. Relaxation of hole density determined from photo-CELIV measurements of B4 sample.

Since the hole photo-CELIV measurements performed using a 355 nm excitation wavelength exhibit complete charge extraction together with more pronounced photocurrent peaks, the calculated μ_h and τ_h values are expected to provide a more accurate description of hole transport and recombination processes in the PVB/stilbene organic blend layer. The corresponding hole photo-CELIV transients are presented in **Figure 27**. The calculated μ_h values, plotted as a function of $t_{\text{delay}} + t_{\text{max}}$, are shown in **Figure 28**, whereas the relaxation behavior of hole density is presented in **Figure 29**.

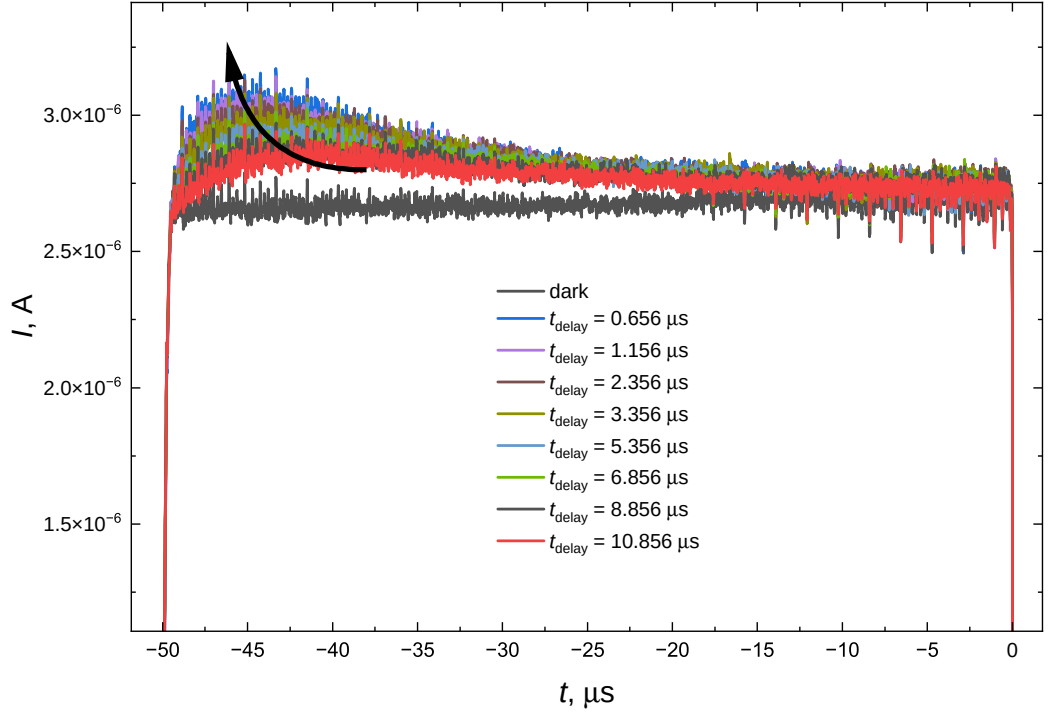


Figure 27. Photo-CELIV hole current transients of B4 sample irradiated with 355 nm wavelength laser pulses. Transients show full charge carrier extraction. The view is zoomed in.

From **Figure 28**, the μ_h values are found to lie in the range of 0.02–0.07 cm²V⁻¹s⁻¹. The mobility dependence on delay time shows trends similar to those presented in **Figure 25**. The exponential decay of hole density (**Figure 29**) indicates a monomolecular recombination mechanism and the τ_h value extracted from the plot is estimated to be approximately 25 μs.

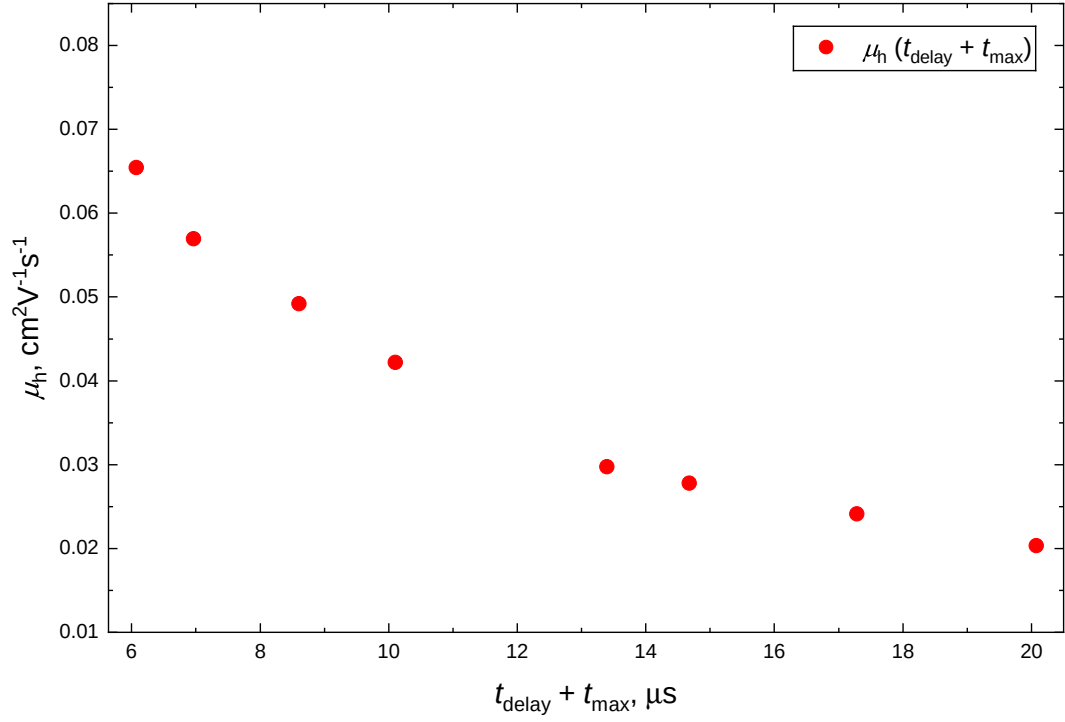


Figure 28. Relaxation of hole mobility determined from photo-CELIV measurements of B4 sample irradiated with 355 nm wavelength laser pulses.

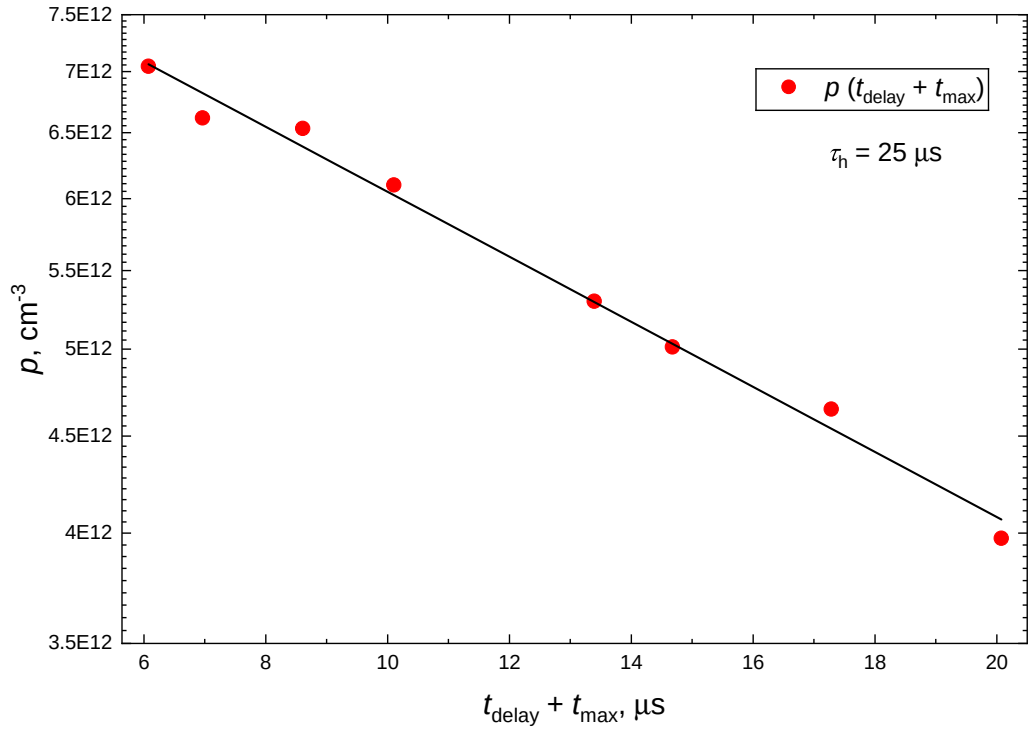


Figure 29. Relaxation of hole density determined from photo-CELIV measurements of B4 sample irradiated with 355 nm wavelength laser pulses.

The electron photo-CELIV current transients are shown in **Figure 30**. It should be noted that, despite the strongly pronounced photocurrent peaks, full charge extraction is not clearly observed in the transients; therefore, only an order of magnitude estimate of the electron lifetime can be determined.

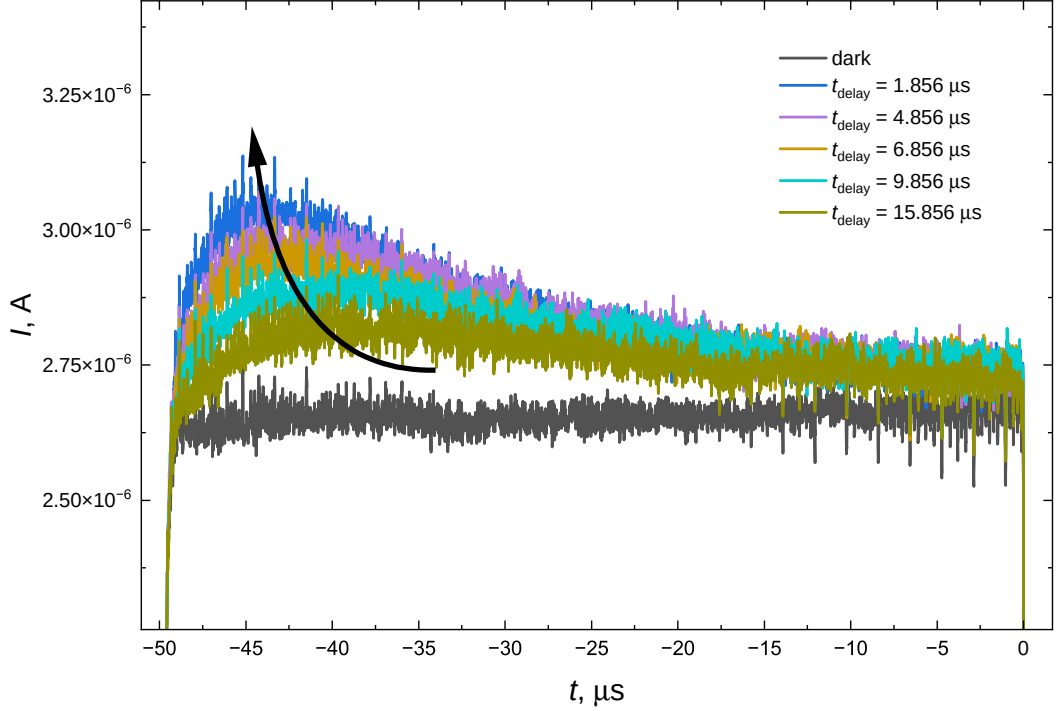


Figure 30. Photo-CELIV electron current transients of B4 sample irradiated with 355 nm wavelength laser pulses. Transients show nearly full charge carrier extraction. The view is zoomed in.

Calculated μ_e values are plotted as a function of delay time in **Figure 31**. The electron mobility exhibits an exponential decrease with increasing delay time, consistent with general energetic relaxation behavior. The μ_e values lie in the range of 0.01–0.05 cm²V⁻¹s⁻¹ and are in good agreement with the measured μ_h values when compared at the same delay time.

From **Figure 32**, which shows the electron density as a function of $t_{delay} + t_{max}$, an exponential fit indicates a monomolecular recombination mechanism and suggests a τ_e value of 37 μs; however, it is more appropriate to state that the lifetime is on the order of tens of microseconds. A difference in determined lifetime values for holes and electrons, here, could be attributed to a difference in experimental conditions.

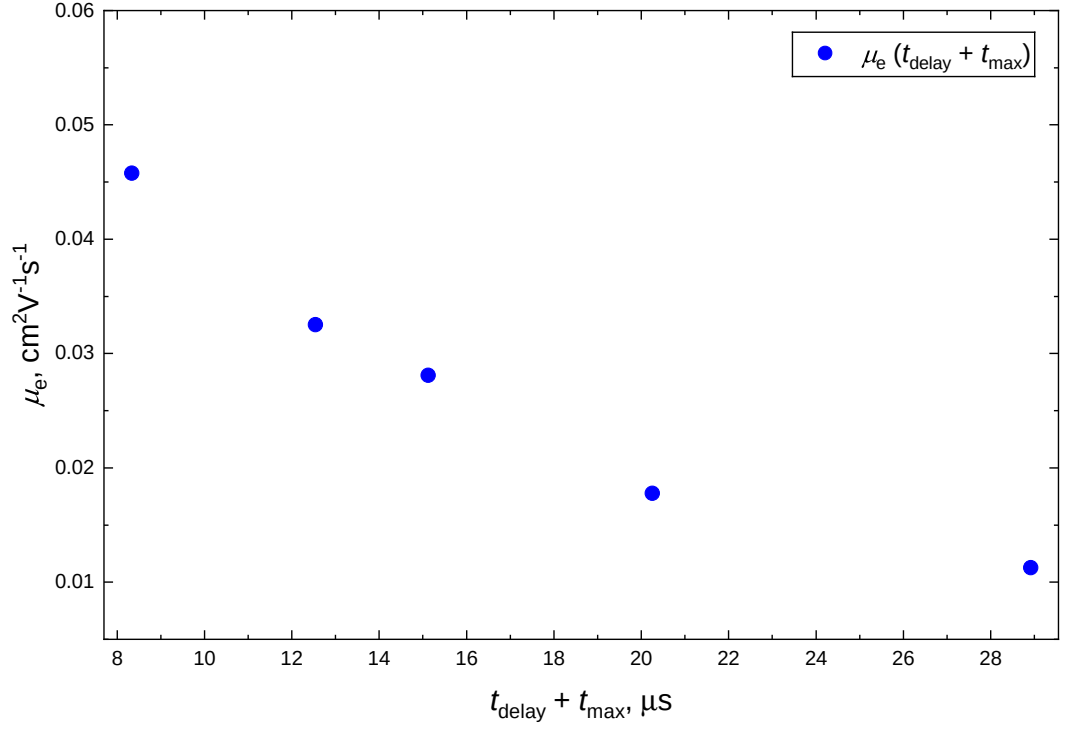


Figure 31. Relaxation of electron mobility determined from photo-CELIV measurements of B4 sample irradiated with 355 nm wavelength laser pulses.

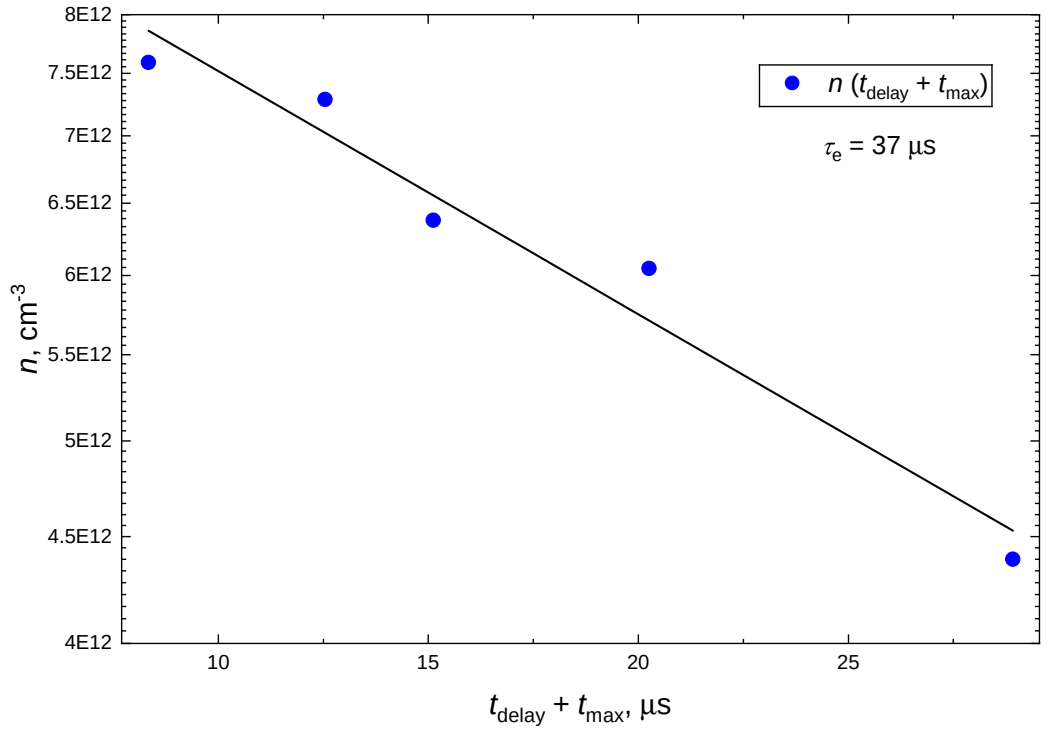


Figure 32. Relaxation of electron density determined from photo-CELIV measurements of B4 sample irradiated with 355 nm wavelength laser pulses.

To summarize the photo-CELIV results, the electron mobility μ_e and hole mobility μ_h in the organic layer containing PVB and stilbene are very similar, with values on the order of $10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. This corresponds to a reduction of approximately two orders of magnitude for holes and one order of magnitude for electrons compared to single-crystal stilbene mobility values reported in the literature [10, 11]. These findings directly indicate somewhat hindered charge transport, arising from increased structural and energetic disorder within the PVB/stilbene layer. Nevertheless, the obtained mobility values remain highly reasonable in the context of organic semiconductors.

Regarding recombination, the observed behavior in the PVB/stilbene organic layer is consistent with a monomolecular process (trap-assisted recombination), with carrier lifetimes τ_e and τ_h on the order of tens of microseconds. In comparison with literature values for single-crystal stilbene, where $\tau < 1 \text{ }\mu\text{s}$ [11], the electron lifetime is increased by at least a few orders of magnitude in the blend system, further indicating enhanced structural and energetic disorder. In addition, for the PVB/stilbene organic layer, the average carrier drift distance before recombination, $\mu\tau E$ can be estimated to be approximately 400 μm (more reliably on the order of hundreds of micrometers). This indicates the capability for long-range charge transport and, consequently, the possibility of substantially increasing the thin-film thickness without significantly reducing charge collection efficiency.

Lastly, a comparison of mobility values between stilbene organic layers containing either PVB or PEPC as the polymer component can, in principle, be made, indicating that layers based on PVB and stilbene exhibit somewhat higher charge carrier mobility values. However, the morphologies formed with both polymers exhibit similar stilbene crystallization within the blend layers and charge carrier transport in both cases occurs predominantly through stilbene, indicating promising characteristics for integration into organic electronic devices.

5 Conclusions

After the analysis of presented results in **Chapter 4**, the following conclusions on the hole and electron charge transport and recombination in organic layers with stilbene crystallites can be stated:

1. Phase separation was controlled by processing in such a manner that results in stilbene/polymer organic layer morphologies, that allow charge carrier transport through the crystallites or crystalline domains of stilbene.
2. The combination of PVB or PEPC polymer with stilbene to form a polymer/small-molecule blend introduces additional structural and energetic disorder, which only slightly reduces the inherently high charge carrier mobility of pure stilbene, thereby establishing a promising pathway for the use of such layers in organic electronic devices.
3. Incorporating stilbene into a PVB matrix extends hole and electron lifetimes to tens of microseconds (compared to $< 1 \mu\text{s}$ for electrons in pure stilbene), while maintaining high charge transport properties in the context of organic materials, thereby establishing a pathway for suppressing recombination through morphology control without significantly hindering charge transport properties.

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KRŪVININKŲ PERNAŠA IR REKOMBINACIJA ORGANINIUOSE SLUOKSNIUOSE SU STILBENO KRISTALITAIŠ

MAGISTRATŪROS STUDIJŲ BAIGIAMASIS DARBAS

Šiame darbe tiriami krūvininkų pernašos ir rekombinacijos procesai organiniuose mišriuose sluoksniuose, sudarytuose iš mažamolekulinio puslaidininkio *trans*-stilbeno ir polimerinių medžiagų – PVB bei PEPC. Nors monokristaliniai organiniai puslaidininkiai pasižymi itin dideliu krūvininkų judriu, jų praktinis pritaikymas yra sudėtingas dėl komplikuoto kristalų auginimo ir sudėtingo integravimo į prietaisus. Todėl organinėje elektronikoje plačiai taikomi apdirbimo iš tirpalų technologiniai metodai, leidžiantys formuoti kristalinius sluoksnius su kontroliuojama morfologija. Tokiuose organiniuose sluoksniuose, polimerai pagerina sluoksnių formavimąsi ir leidžia išlaikyti palankias mažamolekulinių puslaidininkių krūvininkų pernašos savybes.

Šiame tyrime fazių atsiskyrimas stilbeno/polimero mišiniuose buvo kontroliuojamas gamybos metu taip, kad susidarytų morfologijos, skatinančios krūvininkų pernašą per stilbeno kristalitus arba kristalines sritis. Buvo pagaminti dviejų tipų organiniai sluoksniai, naudojant PVB arba PEPC kaip polimerinį komponentą. Abi sistemos, paruoštos iš tirpalų, kuriuose stilbeno ir polimero santykis buvo 4:1, pasižymėjo dideliu kristališkumu. PVB/stilbeno sluoksniuose susiformavo didelės kristalinės sritys be aiškiai matomų ribų tarp kristalitų, tuo tarpu PEPC/stilbeno sluoksniai demonstravo platų pasiskirstymą atskirų kristalitų, kurių matmenys siekia maždaug $600 \times 300 \mu\text{m}$. Rentgeno difrakcijos analizė parodė, kad vyraujančios stilbeno difrakcinės smailės, tiek sluoksniuose su PVB, tiek su PEPC, priklauso tai pačiai kristalografinėi šeimai ir yra tarpusavyje lygiagrečios visame sluoksnyje, kas parodo tvarkingą kristalų išsidėstymą padėklo atžvilgiu.

PEPC/stilbeno sluoksnių elektrinis charakterizavimas buvo atliktas naudojant TOF metodą. Tiek skylių, tiek elektronų judris nustatytas 10^{-3} – $10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ intervale, o elektronų judris buvo nežymiai didesnis nei skylių. Esant didesniems elektriniams laukams, skirtumas tarp šių verčių tapo nereikšmingas. Palyginus su literatūroje pateiktomis monokristalinio stilbeno vertėmis, nustatytas maždaug trimis eilėmis mažesnis skylių judris ir dviem eilėmis mažesnis elektronų judris, kas rodo apsunkintą pernašą dėl mišraus sluoksnio morfologijos sukeltos struktūrinės ir energetinės netvarkos. Nepaisant to, gautos judrio vertės

organinių puslaidininkių kontekste išlieka santykinai didelės, todėl tokios morfologijos yra perspektyvios organinės elektronikos prietaisams.

PVB/stilbeno sluoksnių elektrinės savybės buvo tirtos taikant foto-CELIV metodą. Nustatyta, kad elektronų ir skylių judriai yra labai panašūs ir siekia apie $10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Lyginant su monokristalinio stilbeno vertėmis, šie judriai yra sumažėję maždaug dviem eilėmis skylėms ir viena eile elektronams, o tai taip pat rodo padidėjusią struktūrinę ir energetinę netvarką mišriame sluoksnyje. Nepaisant šio sumažėjimo, krūvininkų pernaša išlieka efektyvi organinių puslaidininkių sistemų kontekste.

Be krūvininkų pernašos, PVB/stilbeno sluoksniuose buvo tiriami ir rekombinacijos procesai. Nustatyta, kad stebima rekombinacija atitinka gaudyklių sąlygotą rekombinacijos mechanizmą, o elektronų ir skylių gyvavimo trukmės siekia dešimtis mikrosekundžių. Palyginus su literatūroje pateikiamomis gryno monokristalinio stilbeno vertėmis, kur krūvininkų gyvavimo trukmė mažesnė nei 1 μs (elektronams), mišrioje sistemoje stebimos žymiai ilgesnės gyvavimo trukmės. Tai rodo, kad morfologijos kontroliavimas polimero/mažamolekulinio puslaidininkio mišiniuose gali efektyviai slopinti rekombinaciją, kartu išlaikant santykinai didelį krūvininkų judrį.

Apibendrinant galima teigti, kad stilbeno integravimas į PVB ir PEPC polimerines matricas sukelia papildomą struktūrinę ir energetinę netvarką, kuri tik iš dalies sumažina itin didelį gryno stilbeno judrį, tačiau leidžia išlaikyti palankias pernašos savybes organinių puslaidininkių taikymams. Tuo pačiu metu PVB/stilbeno sistemoje stebimos pailgėjusios krūvininkų gyvavimo trukmės atskleidžia perspektyvų rekombinacijos slopinimo būdą, paremtą morfologijos valdymu. Gauti rezultatai parodo kontroliuojamos stilbeno/polimero mišrių sluoksnių morfologijos potencialą organinės elektronikos prietaisuose.

Appendix 1

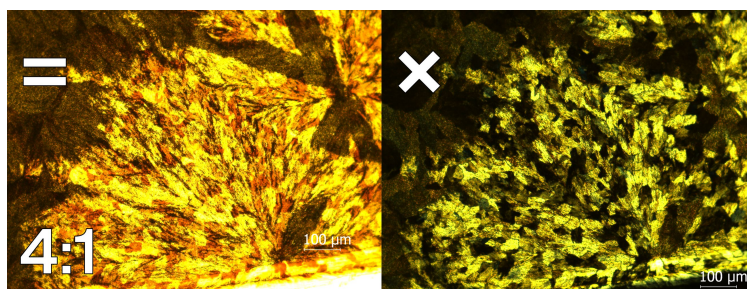


Figure 33. Polarized light microscopy images of organic layer with PC polymer and stilbene crystallites.



P3



P4

Figure 34. P3 and P4 sample photographs.