

Polarisation spectroscopy of thin films of F8BT poly(9,9-dioctylfluorene-alt-benzothiadiazole) polymer

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Received May 13, 2025

Revised June 22, 2025

Accepted June 25, 2025

In this work, the transmission spectra feature of F8BT (poly(9,9-dioctylfluorene-alt-benzothiadiazole)) polymer films were studied, for which significant optical anisotropy was established. The effect of temperature heating and additional irradiation on the anisotropy of optical properties was studied. It was found that UV irradiation leads to a significant increase in the refractive index difference along and across some axis lying in the sample plane. The temperature effect partially attenuates this difference. The observed phenomenon can be explained by the destruction of chemical bonds in polymer chains of poly(9,9-dioctylfluorene-alt-benzothiadiazole).

Keywords: poly(9,9-dioctylfluorene-alt-benzothiadiazole), optical anisotropy, polarization spectroscopy, circular polarization.

DOI: 10.61011/SC.2025.03.61560.8158

1. Introduction

Poly(9,9-dioctylfluorene-alt-benzothiadiazole) (PFBT) is a promising electrically conductive polymer [1], which has attracted the attention of researchers in recent years due to its unique optical properties and potential applications in the field of organic electronics and photonics [2]. The complex structure of PFBT, consisting of fluorene and benzothiadiazole units, provides it with outstanding performance [3,4], such as its high photoconductivity and excellent optical properties, making it an ideal candidate for use in organic light-emitting diodes (OLED) [5], solar cells [6] and other optoelectronic devices [7,8].

One of the key features of PFBT is its ability to efficiently absorb light in the visible range, due to the presence of benzothiadiazole groups that contribute to the formation of intermediate energy levels. These levels allow the polymer to interact effectively with photons, which leads to an increase in its fluorescent properties [9]. An important aspect is also the high quantum efficiency of fluorescence, which makes PFBT particularly attractive for the development of highly efficient LEDs and lasers based on organic matter [10].

The optical properties of PFBT can vary significantly depending on the synthesis and processing conditions of the material [11–13]. For example, changes in temperature, solvent [14], polymerization time, and other parameters can significantly affect the morphology and, consequently, the optical characteristics of the polymer [15,16]. Therefore, a detailed study of the effect of these factors on the absorption and fluorescence spectra of PFBT is necessary to optimize its use in various devices [17].

In recent years, there has been a growing interest in organic polymers as an alternative to traditional inorganic materials in the field of photonics and electronics [18]. Organic materials such as PFBT have a number of advantages, including the flexibility [19], lightness, and the ability to operate at low temperatures. These characteristics open up new horizons for the creation of lightweight and compact devices that can be integrated into various devices, from displays [20] to solar panels [21,22].

Despite the promising properties of PFBT, there are a number of issues regarding its stability and durability under operating conditions. Studies show that exposure to external factors such as light, temperature, and chemicals [23] can strongly affect the optical properties of the polymer. Therefore, it is important not only to study the optical characteristics themselves, but also to develop strategies to increase the resistance of PFBT to external influences.

Studying the optical properties of PFBT opens up new horizons for innovative applications in organic electronics and photonics [24,25]. Understanding the mechanisms underlying its optical behavior will not only optimize existing technologies, but also develop new devices that can significantly change the market and improve the quality of life [26,27].

We studied in this article in detail the transmission spectra of polarized light through poly(9,9-dioctylfluorene-alt-benzothiadiazole) depending on the synthesis conditions. The Stokes parameters of the light transmitted through the sample were measured. The effect of heating and additional radiation on the optical properties has been studied.

2. Experiment

This paper studied in detail the films of F8BT (poly(9,9-dioctylfluorene-alt-benzothiadiazole)) deposited on a glass substrate with a transparent conductive layer of ITO (indium tin oxide) using two different methods: spin-coating (SC) and drop-casting (DC). The spin-coating method consists in evenly distributing the polymer solution over the surface of the substrate by rotating it at high speed. This method allows creating thin films with a high degree of uniformity. A schematic representation of the section of the sample obtained by this method is shown in Figure 1, *a*. The polymer solution is applied to the substrate as a drop in the drop-casting method. The resulting films, as a rule, have a greater thickness and a less uniform structure compared to films created by centrifugation. Schematically, the section of such samples is shown in Figure 1, *b*.

The structural formula of F8BT (Figure 2) includes long alkyl chains that ensure good solubility of the polymer in organic solvents. This property plays a key role in the possibility of forming thin films by wet application.

The optical properties of F8BT films were studied using the transmission spectra of polarized light. The dependences of the transmission spectra of the sample, as well as the effect of thermal heating and additional irradiation, have been studied. Linearly polarized light fell on the sample, and the transmission spectra and Stokes parameters of the light passing through the sample were measured. The measurements were carried out using a spectrometer with a focal length of 0.5 m equipped with the CCD detector Andor iDus DU401A-BV. The main focus was on the visible region of the spectrum.

To study the effect of additional optical irradiation on the characteristics of the sample, laser light sources with wavelengths of 200, 404, 450, 532, and 680 nm were used. The measurements revealed how additional radiation affects the Stokes parameters, which characterize the change in the polarization of light after passing through the sample.

Figure 3, *a* shows an image of the surface of a sample obtained by drop casting DC. It can be seen from the drawing that the sample is not completely homogeneous and has different thicknesses in different places. Figure 3, *b* shows the signal of light transmission through this sample placed in crossed polarizers. The presence of light transmission through the sample under these conditions indicates the presence of significant optical anisotropy.

Figure 4 shows the transmission spectrum of F8BT films. The position of the absorption edge in this spectrum practically coincides with the effective band gap of the material, which is determined by the difference between the energies of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). Values given in the literature: HOMO = -5.9 eV, LUMO = -3.3 eV [3]. The transmission spectra of the samples produced by the SC and DC method coincided.

The main objective of the paper was to study the dependence of the anisotropy of the transmission spectra of



Figure 1. Sample structure. The ITO conductive substrate is coated with a F8BT polymer film. *a* — sample obtained by spin-coating (SC); *b* — sample obtained by drop casting (DC). The thickness of the films was 200–500 μm .

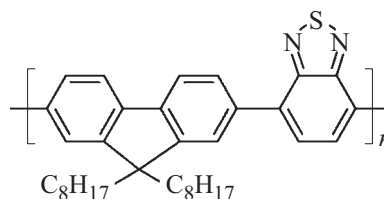


Figure 2. The chemical formula is F8BT poly(9,9-dioctylfluorene-alt-benzothiadiazole).

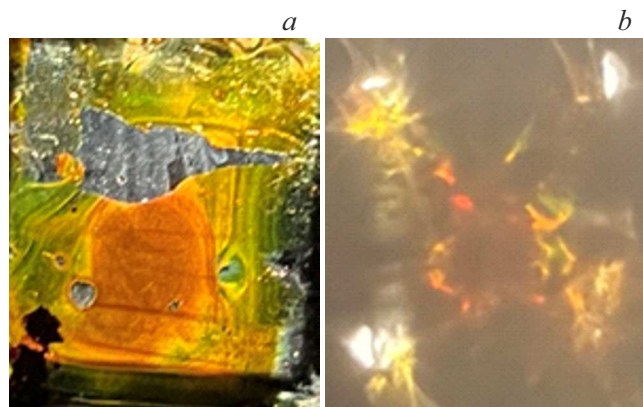


Figure 3. *a* — image of DC sample. *b* — a light transmission signal through a sample placed between polarizers crossed relative to each other.

films on temperature and additional irradiation. The greatest effect on the anisotropy of optical properties was manifested under the shortest wavelength irradiation. A laser with a wavelength of ~ 200 nm, was used for UV irradiation. Different doses of radiation were used: 25, 600 and 1500 mJ. After UV irradiation, the samples were subjected to thermal annealing at a temperature of 200 $^{\circ}\text{C}$ for 40 and 80 minutes.

The degree of circular polarization of light transmitted through a sample produced by drop casting was studied both before and after UV irradiation; after UV irradiation and subsequent annealing at 200 $^{\circ}\text{C}$ for 40 minutes; and also after UV irradiation and subsequent annealing at 200 $^{\circ}\text{C}$

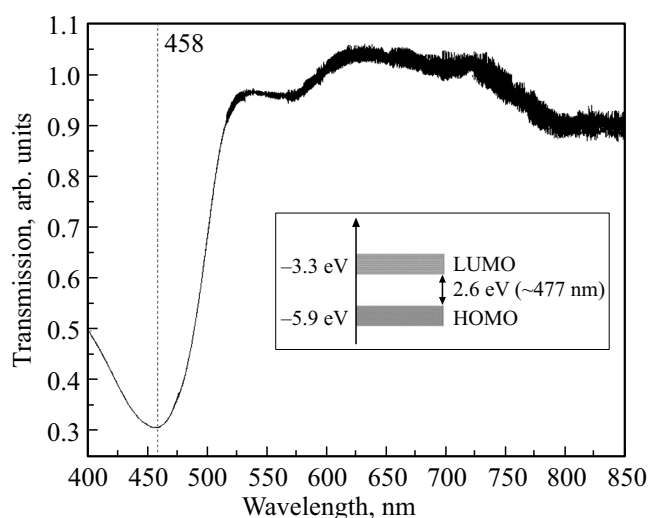


Figure 4. Transmission spectrum of a sample produced by centrifugation SC. The energy diagram of electronic states is shown on the inset.

for 80 min. It was found that UV irradiation leads to a significant increase in the optical anisotropy of films. Subsequent annealing of the polymer contributed to the partial restoration of the isotropy of the films (Figure 5).

Studies have shown that the degree of changes in the optical properties of films directly depends on the dose of UV radiation. For example, a sample subjected to a lower dose (600 mJ, Figure 5, *a*) shows less pronounced changes in optical properties compared to a sample that received a higher dose (1500 mJ, Figure 5, *b*). Further annealing in the case of weak irradiation leads to increased anisotropy, rather than partial restoration of the initial properties of the material, as in the case of stronger irradiation. The samples

produced by the DC method showed a greater effect of irradiation on the amount of optical anisotropy, especially at the edges of the sample, than the samples obtained by SC.

In the sample, an axis lying in its plane was revealed, relative to which the degree of circular polarization reaches a maximum at an angle of 45° between the direction of linear polarization of the incident light and this axis, and is minimal when the polarization vector coincides with the axis. The dependence of the degree of circular polarization of transmitted light on the angle between the direction of linear polarization and the specified axis was measured. Figure 6, *a* and *b* show the spectral dependences of the degree of circular polarization on the angle between the axis and the direction of polarization. It can be seen that the degree of polarization changes sign when the angle is changed by 90° .

3. Discussion of the results

The results obtained indicate that optical anisotropy initially occurs in the sample, which manifests itself in the birefringence effect, which leads to the conversion of linear polarization into circular polarization when light passes through the sample. Indeed, the linear chains of this polymer are elongated. This is manifested in the macroscopic anisotropy of the entire sample. Due to the presence of flat benzene rings, polymer chains form a layered structure in which neighboring layers interact with each other through Van der Waals forces and tend to align in the same direction. Chains located in adjacent layers may be slightly rotated relative to each other due to the weak coupling between the layers. Due to their great length, it is difficult for them to line up strictly parallel or antiparallel to each other.

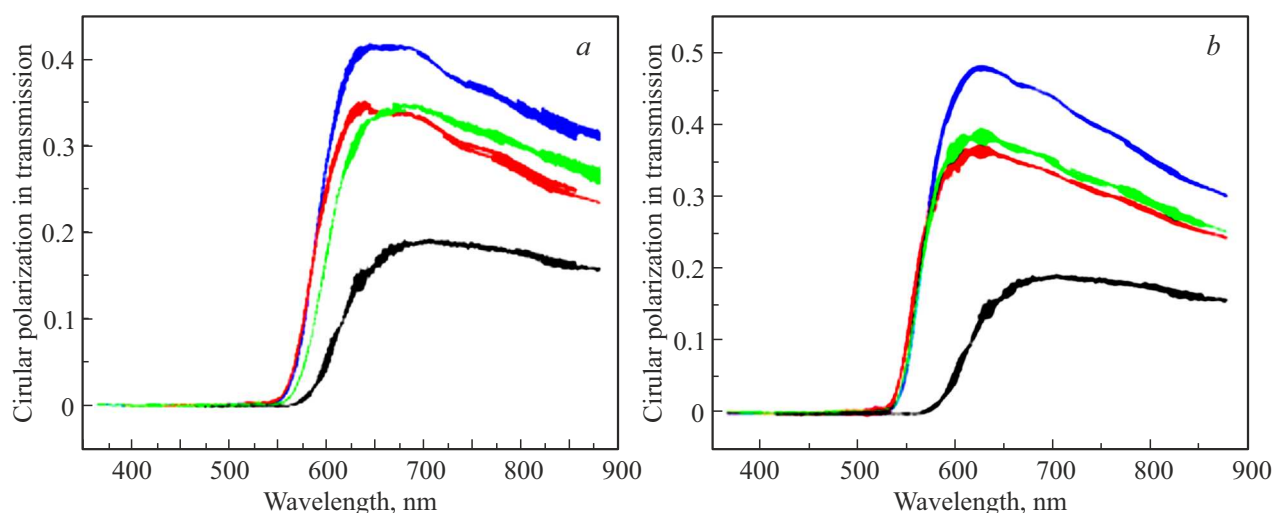


Figure 5. The dependence of the degree of circular polarization of the light transmitted through the sample on UV radiation and temperature exposure, taken at two separated points of the sample. Black curve — before irradiation and heating, blue curve — after UV radiation with a dose of 600 mJ (*a*) and 1500 mJ (*b*), red curve — after 40-minute annealing, green curve — after 80-minute annealing at a temperature of 200°C .

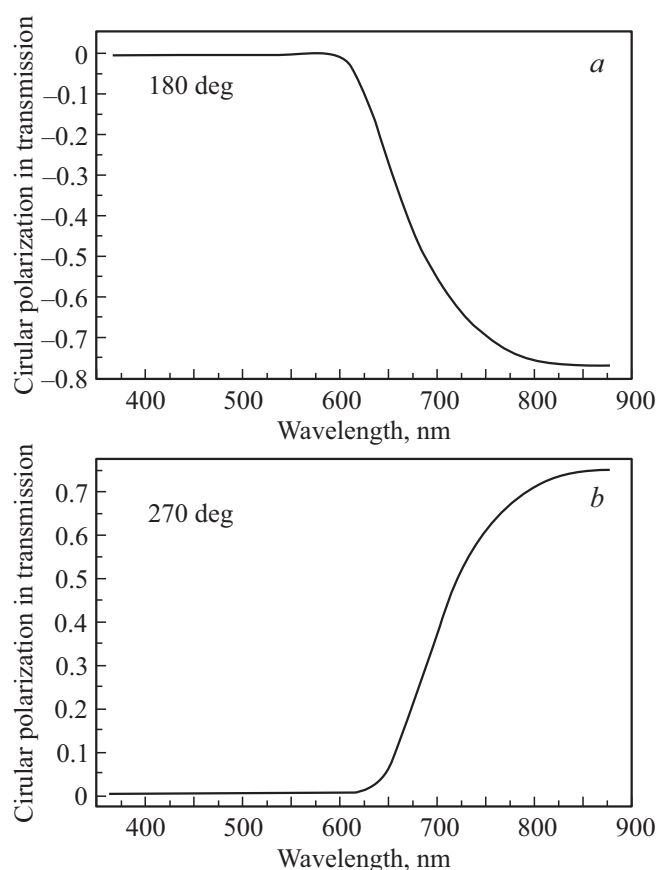


Figure 6. Dependence of the degree of circular polarization of transmitted light *a*) for the angle between the detected axis and the direction of linear polarization of incident light, equal to 180° , and *b*) for angle 270° .

UV irradiation causes the breaking of covalent chemical bonds in long polymer chains and the formation of shorter fragments. These fragments are easier to adjust to each other, which is manifested in an increase in optical anisotropy. Strong anisotropy can be an energetically less favorable state of matter, which usually manifests itself as the formation of a domain structure.

During thermal annealing, polymer molecules tend to occupy positions corresponding to the minimum energy, which is manifested in a slight decrease in anisotropy.

4. Conclusion

According to the measured degree of circular polarization of transmitted light through films of F8BT poly(9,9-dioctylfluorene-alt-benzothiadiazole) polymer, their optical anisotropy was established. The anisotropy was especially pronounced for samples obtained by drop-casting (DC). The effect of thermal heating and additional irradiation on the anisotropy of optical properties was studied. It was found that UV irradiation leads to a significant increase in the difference in refractive indices along and across the axis in

the sample plane. The temperature effect partially weakens this difference. The observed phenomenon can be explained by the breaking of covalent chemical bonds in long polymer chains under UV irradiation and by facilitating the mutual orientation of shorter chains.

Funding

L.V. Kotova and A.M. Smirnov express their gratitude to the Russian Science Foundation for financial support (grant No. 23-72-10008).

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by A.Akhtyamov