

Thermoelectric generators are among the most promising sources of energy: they do not contain moving parts, do not consume liquids or gases, and can also use heat dissipated in the atmosphere [1]. In recent years, the search for new thermoelectric materials, in particular, polymer materials, has been actively conducted. Polymer conducting materials have a rather low Seebeck effect relative to metals or alloys, but polymers are cheaper to produce (solution technologies can be used), they are lighter in weight and can be applied to most surfaces. An important feature of polymers is the ability to adjust their functionality by varying the polymer composition and film preparation conditions [2].

Although such devices usually lose out in efficiency to those based on metal alloys, they may have other advantages. For example, organic thermoelectric polymer materials make it possible to produce compact devices using the technology of applying them in the form of thin films from a solution. Such organic materials can be applied to flexible substrates using a continuous process at normal temperatures, which allows for very high productivity with minimal material consumption. For these reasons, thermoelectric cells have great potential for producing low-cost renewable energy sources that can have a large footprint. Separately, it is worth noting the possibility of layer-by-layer deposition of polymer and inorganic layers, as well as electrodes and thermocouples to obtain hybrid devices with an increased Seebeck effect.

However, to date, most of the known organic systems have a rather low thermoelectric effect, which is due to the suboptimal morphology and structure of the interphase boundaries, which lead to a decrease in the mobility of charge carriers in the direction of the temperature gradient. One of the ways to control the structure and thermoelectric properties of such systems is to select the sample preparation conditions. Examples of such conditions include solvent selection, thermal prehistory, the possibility of annealing in solvent vapor, and the use of various substrates. X-ray scattering techniques are traditionally used to control the structure in thin films.

## Materials and methods

### Materials

The commercial polymer PNDIT2 produced by Oscilla (Figure 1a) was used as the studied systems, as well as two completely new polymers specially synthesized within the framework of the project, which have high prospects for research. These polymers were designated as P1 and P2, and the diagrams are shown in Figures 1b and 1b, respectively. For these polymers, it is proposed to study the phase behavior and relate it to the structure and properties.

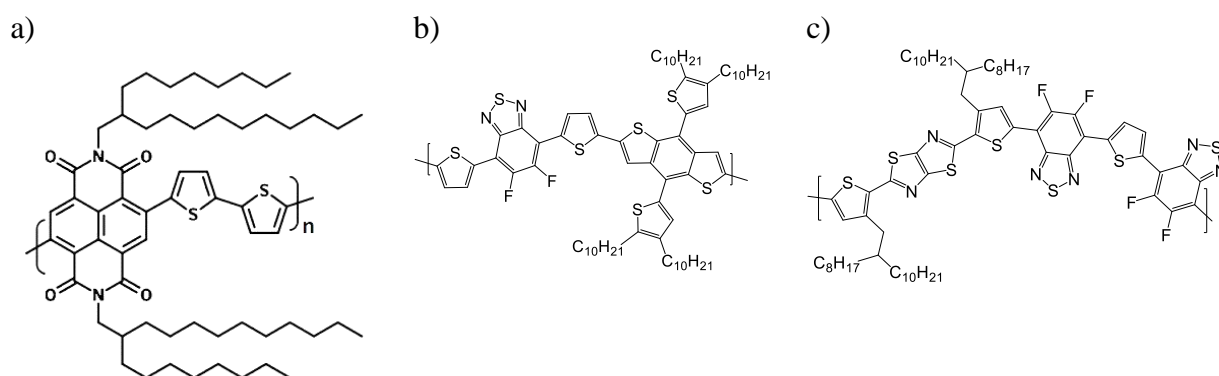


Figure 1-Chemical structures of PNDIT2 (a), P1 (b), and P2 (c) polymers.

### Preparation of thin films

For the production of thin films of samples, solutions with a concentration of 20 mg / ml were prepared in chloroform for samples P2 and P1 and in chlorobenzene for sample PNDIT2. All samples have good solubility, but for the best solubility, these solutions were placed on the heating platform of an IKA magnetic stirrer at elevated temperature with a stirring element for 2 hours. The samples were applied to pre-cleaned 1.5x1.5 cm silicon wafers by spin-coating at a speed of 1000 rpm, the sample amount was 50 microns per drop.

### Results and discussion

Data on the structure during heating and annealing of conjugated polymer samples are shown in Figures 3-5. The selected reference sample of the PNDIT2 polymer is well described in the literature, and the structure of this polymer has already been measured before and by the

authors of this paper. When this sample was deposited, the structure corresponding to which the diffractogram is shown in Figure 2 was obtained. Annealing of this sample at 120 ° C did not lead to significant changes, but a narrowing of the peaks can be observed, which may indicate a better packing of molecules. The peak seen in the meridional direction at 4.1 Å corresponds to the intermolecular distance (pi-pi stacking) of the molecules lying in the film plane, which corresponds to the packing geometry of the conducting layer stretched along the film. Two peaks at the equator in the region of 23.2 and 13.2 Å are also visible, which correspond to the ordering of long rigid sections of molecules along the longer direction of the rigid block, and also describe the effect of flexible alkyl junctions. The orientation of the peaks indicates that the film texture corresponds to a flat-on geometry when the plane of the conjugate fragments is parallel to the film plane. This orientation of the molecules ensures high charge mobility in the direction normal to the film.

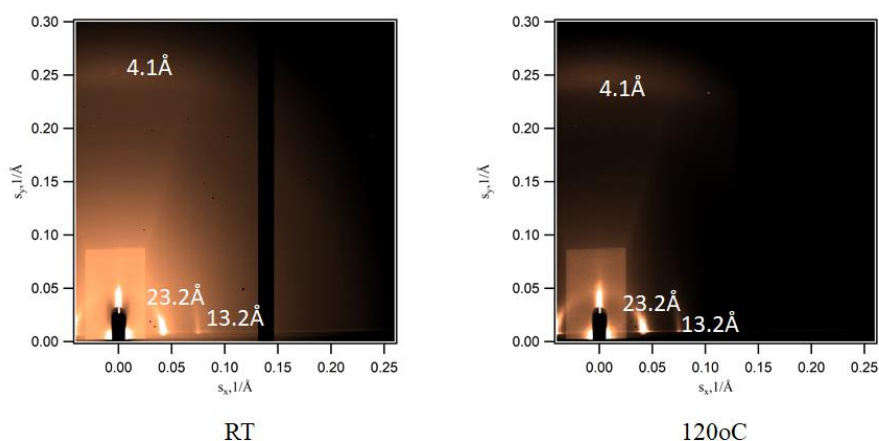


Figure 2 – two-dimensional PNDIT2 diffractograms obtained at different temperatures (RT on the left, 120oC on the right).

X-ray diffraction analysis of samples P1 and P2 shows a different picture. For sample P1, an intense meridional peak is observed at 20.1 Å corresponding to a layered lamellar liquid crystal package parallel to the film surface (Fig. 3). Annealing shows the appearance of several orders of magnitude of this peak, which is associated with an improvement in lamellar morphology. The absence of an intense pi-pi stacking peak indicates weak packing of molecules in the layer. The P2 film diffractograms show a single order of meridional lamellar peak even after annealing at 180 ° C (Figure 4). An equatorial peak of 3.6 Å is present, indicating a regular packing of conjugate fragments and side chains along the layer. Such an edge-on texture should ensure efficient transport of charge carriers along the film.

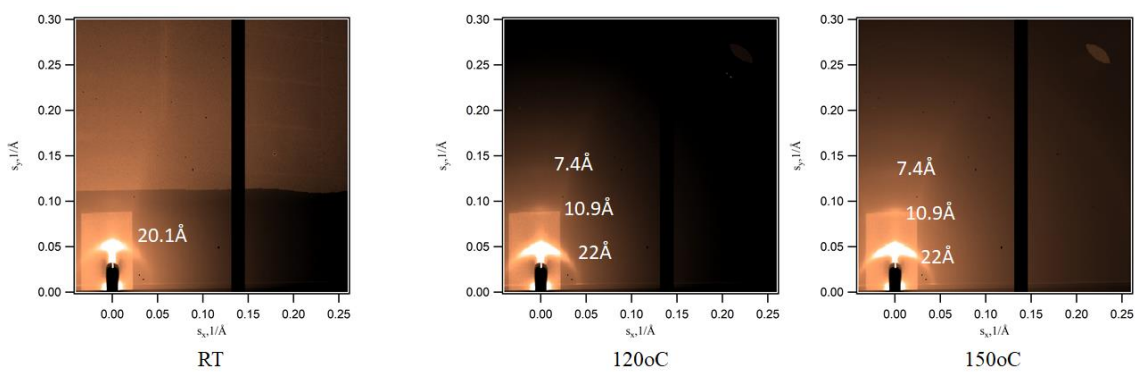


Figure 3 – two-dimensional P1 diffraction patterns obtained at different temperatures (RT on the left, 120oC in the center, 150oC on the right).

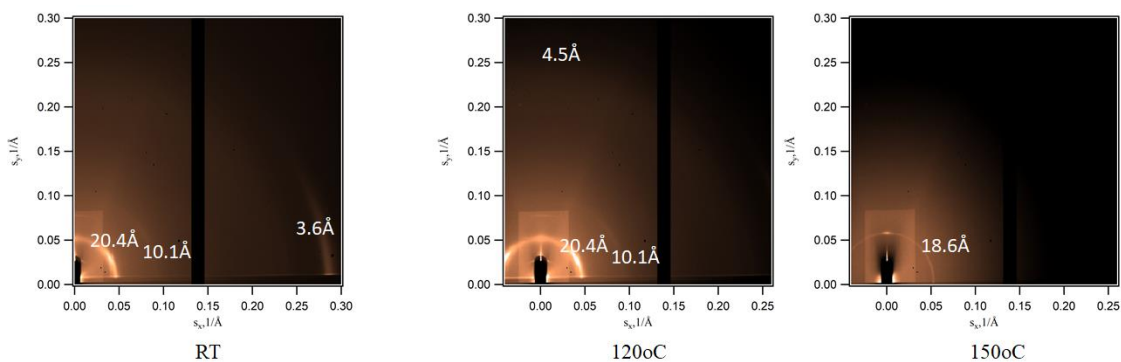


Figure 4 – two-dimensional P2 diffraction patterns obtained at different temperatures (RT on the left, 120oC in the center, 150oC on the right).

## conclusion

In this work, the texture of thin films of thermoelectric polymers was studied at various annealing temperatures. The orientation of conjugated fragments relative to the substrate is compared for two polymers synthesized at this stage of the project: based on alternating units of benzodithiophene, 2,7-carbazole, and benzothiadiazole (P1) and based on alternating units of thiazolothiazole, bitiophene, and benzothiadiazole (P2) with a commercially available organic conjugated polymer (PNDIT2). It is shown that all the polymers under study demonstrate the formation of an ordered liquid crystal texture, and optimal annealing temperatures are selected for each system. X-ray diffraction data show that, depending on the chemical structure of the polymer, the orientation of conjugated fragments of the main chain can be either parallel (flat-on) or normal (edge-on) with respect to the substrate. This makes it possible to vary the direction of effective transport of charge carriers and, thus, to manufacture thermoelectric devices of various geometries. In addition, the liquid crystal nature of thin films opens up opportunities for increasing the size of ordered domains in the film plane during high-temperature annealing and improving the Seebeck effect in thermoelectric devices based on these polymers by reducing the number of interfacial boundaries in the active layer.

1. Q. Zhang, Y. M. Sun, W. Xu, D.B. Zhu *Adv. Mater.*, 2014, 6829
2. O. Bubnova, Z. Ullah Khan, A. Malti, S. Braun, M. Fahlman, M. Berggen, X. Crispin *Nature Mat.*, 2001, 10, 429