Właściwości optyczne oraz elektryczne nowych polimerów i kopolimerów pochodnych polipirolu

rozprawa doktorska

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Abstrakt

Research that provides information on new possibilities for the practical application of organic systems is essential for the development of electronics needed in modern society.
The doctoral dissertation presents the results of a study of the optical and electrical properties of new polymers and copolymers derived from polypyrrole, which could have applications in electronic circuits.

The main objective of the dissertation was to search for new and promising polymer systems. One of the side goals was to study the effect of electron-donor and electron-acceptor substituents on the properties of the electronic structure. In the dissertation, the most promising polymeric systems designed by theoretical means were synthesized and characterized by experimental methods. An essential aspect of the work was to find correlations between the results of theoretical calculations and those obtained experimentally for the group of compounds studied.

The research objects presented in the dissertation are a group of polymers and copolymers that are polypyrrole derivatives. The functionalization of polypyrrole with methyl and carboxyl groups was performed to improve its optical and electrical properties. In addition, doping of the obtained polypyrrole derivatives was carried out.

Combustion analysis, differential scanning calorimetry, thermogravimetric analysis, scanning electron microscopy, and energy dispersive X-ray spectroscopy were used to characterize the resulting polymers. Raman spectroscopy, infrared spectroscopy, electron paramagnetic resonance, and impedance spectroscopy were used to study optical and electrical properties. Theoretical analysis of electrical and optical properties was carried out using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods.

The first part of the dissertation presents the results of theoretical calculations on the effect of functional groups on the optical and electrical properties of polypyrrole derivatives. It is shown that the effect of substituted CH_3 groups on the electron structure is negligible, while substitution with COOH groups causes, among other things, a narrowing of the energy gap and changes in the energy positions of the HOMO and LUMO levels.

The results of theoretical studies of donor-acceptor systems and analysis of the effect of dopants on polymer systems have shown that the most promising sequences are those of donor-acceptor quatromer systems with the most extended possible donor and acceptor fragments. For such systems, the most significant shift of the HOMO→LUMO transition

toward lower energies is observed. It is shown that the doping process affects the electron structure, which is evident in theoretical electronic spectra.

The next part of the doctoral thesis presents experimental results on the obtained polymers and copolymers. The values of specific electrical conductivity for the studied systems and charge jump activation energies were determined below 0.7 eV for the studied group of compounds. The obtained materials are characterized by 3D conductivity. Energy gaps were also determined for the tested materials. The charge carriers in the polymers studied were shown to be polaron or bipolar. Studies of polypyrrole derivatives have shown that introducing carboxyl groups into the polymer affects the electronic structure.

The final section of the dissertation presents correlations of experimental and theoretical results. It was shown that there is a correlation between electron excitation energies obtained theoretically and experimentally. Results obtained for doped systems show that predictions by DFT methods of energy positions differ by 0.5 - 1.0 eV from what is observed experimentally.