

New Poly(arylene thiophenes)

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Soluble poly(arylene thiophenes) containing amide bridge bonds and free nitrile groups have been synthesized through polycondensation of new arylene-bis(2-aminothiophene-3-carbonitrile)s with arylene-dicarboxylic acid dichlorides, and their physical and photochemical properties have been studied.

Keywords: Organic Conductors and Semiconductors, Light-Emitting Diodes, Arylene-bis(2-aminothiophene-3-carbonitrile)s, Gewald Reaction, Thiophene-containing Polyamides.

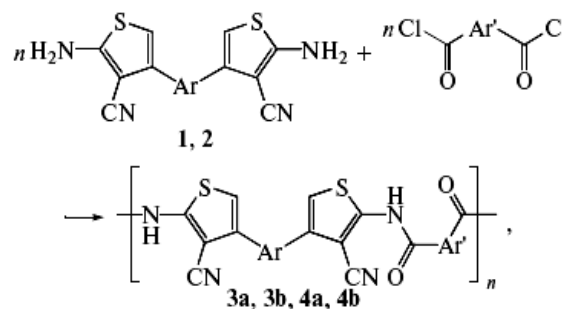
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Thiophene-containing polymers, primarily polythiophene and its derivatives, have attracted the attention of researchers owing to their wide spectrum of properties, such as conductance, luminescence, and electroluminescence [1–3]. These properties predetermine their possible application as organic conductors and semiconductors [1–4], light-emitting diodes [1, 5], sensors [1, 4], etc. However, the infusibility and insolubility of polythiophenes make them difficult to process and restrict their practical applications. The processability of thiophene-containing polymers may be improved via incorporation of hinge bridge fragments into their chains [6]. However, simultaneously with improved processability of rigid-chain polymers, the incorporation of hinge bridge fragments into the structure of rigid-chain polymers may lead to the breakage of their conjugation chains and deterioration of their electrophysical properties. Therefore, from our point of view, the most promising method includes the incorporation of bridge fragments that will not break the conjugation chain or that will restore it through polymer-analogous transformations in the course of processing.

Earlier, we synthesized new arylene-bis(2-aminothiophene-3-carbonitrile)s (1) and (2) [7] via the Gewald reaction. In our opinion, these compounds are promising as monomers for the synthesis of thiophene-containing polymers characterized by improved processability and the ability to form poly-conjugated structures. At the same time, the presence of nitrile groups in thiophene fragments is interesting from the standpoint of both the synthesis of polymers with new photoelectric properties and the feasibility of their subsequent chemical transformations. In this study, we investigated the synthesis of polythiophenes with main-chain acrylamide groups via the interaction of compounds (1) and (2) with arylene-dicarboxylic acid dichlorides. At the first stage, we elaborated the procedure for the synthesis of nitrile-substituted thiophene-containing polyamides (3f0, (3b), (4a) and (4b): were Ar = (1, 3) 1,4-phenylene or 4,4'-biphenylene and Ar' = (a) 1,4-phenylene or (b) 1,3-phenylene.

The low-temperature polycondensation of compounds (1) and (2) with tere- and isophthaloyl dichlo-

rides was performed in DMAA because it is a good solvent for the above polyamides and, at the same time, serves as an acceptor of hydrogen chloride released during the reaction [8, 9].



The polycondensation is difficult to perform at room temperature, because of the partial solubility of diamines (1) and (2) in DMAA. Obviously, the synthesis proceeds through the formation of soluble polyamides on the diamine surface. Polymers (3a), (3b), (4a) and (4b) resulting from this reaction are, according to X-ray diffraction analysis, yellow-brown amorphous powders with reduced viscosities of 0.11–0.18 dl/g that are soluble in amide solvents. The molecular mass of polymer (4b), as measured by the sedimentation method, is 2.2×10^3 .

According to the TGA data, polymers (3) and (4) are stable in air up to ~ 300 °C and completely decompose with no carbon residue by a temperature of 550 °C.

When solutions of polyamides (3) and (4) are applied onto a substrate, they form films. The study of the photochemical properties of these polymers showed that their absorption maxima are in the range 413–473 nm, while the emission maxima are observed at 440–475 nm, thus corresponding to the blue region of visible light.

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REFERENCES

1. Conjugated Polymers: *The Novel Science and Technology of Highly Conducting and Nonlinear Optically Active Materials*, Ed. by J.L. Bredas and R. Silbey (Kluwer Academic, Dordrecht, 1991).
2. Electronic Materials: *The Oligomer Approach*, Ed. by K. Mullen and C. Wegner (Wiley-VCH, New York, 1998).
3. Handbook of Oligo- and Polythiophenes, Ed. by D. Fichou (Wiley-VCH, Weinheim, 1999).
4. *Handbook of Organic Conducting Molecules and Polymers*, Ed. by H.S. Nalwa (Wiley, New York, 1997).
5. K. Gurunathan, A.V. Murugan, R. Marimuthu, et al., *Mater. Chem. Phys.* **61**, 173 (1999).
6. E.N. Rodlovskaya, N.G. Frolova, E.D. Savin, and V.I. Nedel'kin, *Polymer Science, Ser. C* **48**, 58 (2006).
7. E.N. Rodlovskaya, N.G. Frolova, E.D. Savin, and V.I. Nedel'kin, RF Patent No. 2 230 743 (2004).
8. V.M. Savinov and L.B. Sokolov, *Vysokomol. Soedin.* **7**, 772 (1965).
9. S.V. Vinogradova, V.V. Korshak, Ya.S. Vygodskii, and V.I. Zaitsev, *Vysokomol. Soedin., Ser. A* **9**, 653 (1967).