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Copolymerization of Pyrrole with Aromatic Bisdiazonium Salts

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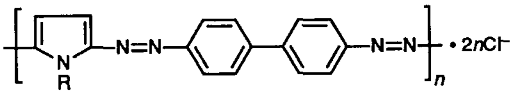
Pyrrole–azophenylene copolymers have been obtained by spontaneous copolymerization of pyrrole with aromatic bisdiazonium salts.

Conjugated polymers have been of interest to many research groups during the past ten years. At the present time polypyrrole is one of the more closely studied polymers of this class and has found practical application as electroactive material.[1] Another type of polyconjugated polymer, polyazophenylene, has demonstrated rather weak conductivity, but is of great interest from the point of view of electrochromic and photochromic properties.[2] The preparation of pyrrole–azophenylene copolymers thus seemed an interesting and attractive aim in synthetic polymer chemistry.

We report here a method of producing pyrrole–azophenylene copolymers by azo coupling of aromatic bisdiazonium salts (BDS) with pyrrole (py). The reaction of py with phenyldiazonium chloride is well known[3,4] for the formation of azo dyes. We have found that the addition of py [dropwise, as hot vapour or in solution ($c = 0.5$–1.0 mol dm^{-3}) in a water-immiscible organic solvent] to a cooled (to 0–5 °C), freshly diazotized aqueous solution of BDS based on benzidine ($c = 0.5$–1.0 mol dm^{-3}, pH = 1–5) results in the instantaneous formation of bright, reflective polymeric films on the surface of the BDS solution. Films removed from the surface of the reaction solution were a green–golden colour on one side, on the other side they were smooth black. The films were characterized by good physico-mechanical properties. A process of saturation of the black dispersive powders took place within the reaction mixture itself upon mixing equimolar amounts of the monomers (yield of polymer reached 95%). The other product of the reaction was a violet dye. In order to remove any traces of the dye the film and powder were simultaneously washed with acetone, ethanol and dimethylformamide under reflux.



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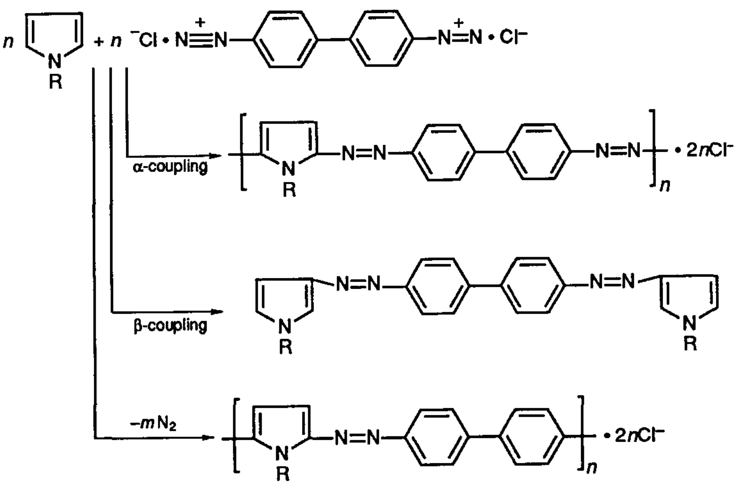
Data obtained from elemental analysis, IR spectroscopy and differential thermal analysis (DTA) have shown the identity of the chemical structures of the films obtained by interphase copolymerization on the surface of the reaction system and of the powders obtained in the reaction mixture. The proposed structure of the polymer **1** is as follows.† DTA studies of the polymer have shown: T (beginning of decomposition) 240 °C, T (5% weight loss) 350 °C, T (19% weight loss) 430 °C; 19% weight loss corresponds to full decomposition of the pyrrole units. The IR spectrum of the copolymer is characterized by well-resolved absorbance bands: ν/cm^{-1} 695w and 760w (C—H vibrations of monosubstituted benzene rings), 820, 1002 (C—H of *para*-substituted benzene rings), 1485 and 1600 (aromatic C═C bonds), 1240 and 1540 (pyrrole C═C bonds) and 1170 (C_{Ar}—N═).[5] It is known that the azo group —N═N— is very difficult to identify due to the overlap of its absorbance bands with those of the aromatic rings.



Scheme 1

Changing the reaction conditions (phase conditions, order of addition of reagents, temperature) led to the formation of other reaction products. Thus, if py is added to the aqueous BDS in a water-miscible solvent ($c = 0.5$–1.0 mol dm^{-3}) such as ethanol or acetone, acetonitrile polymeric films do not form and the main products of the reaction are dyes. Reversing the order of monomer addition also prevents the formation of polymer.

The reaction is thought to proceed as follows (Scheme 1). It is known that diazotization takes place at the α-position of pyrrole at a higher rate than to the β-position. α-Azo dyes are very unstable products in comparison with the β-products.[4] Hence, we suggest that formation of the polymer takes place due to electrophilic attack by the diazo group at the α-position of pyrrole. The high reactivity of the α-form of diazocoupled py and the bifunctionality of BDS are responsible for the instantaneous character of the copolymerization. Diazocoupling of py in the β-position leads to the formation of a very stable, non-reactive form of β-azo dye. The possible influence of solvent on the correlation of α- and β-forms may be explained by the solvation effect. The stronger nucleophilic centre at the α-C atom of py is solvated by solvent molecules. The diazonium cation, being a weaker electrophilic agent in comparison with inorganic M^{n+} ions or an anode surface (in the case of electrochemical polymerization) reacts with py in the β-position.

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† This structure is in good agreement with the elemental analysis data.

It should be noted that at room temperature (20–25 °C) py causes a deazotization reaction which leads to the formation of polymers with mixed irregular structures. Polymers obtained under such conditions consist of py, phenylene with partly included azo groups and oxyphenylene units.

In conclusion, the described method of copolymerization of pyrrole with aromatic bisdiazonium salts allows us to obtain polyconjugated copolymers which demonstrate typical semiconducting properties. The electrical conductivities, measured by a standard four-probe technique for both films and powders (pressed into pellets), were about 10^{-6} S cm^{-1}.

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References

1 See, for example: *Handbook of Conducting Polymers*, Vol. 1 and 2, ed. T. Skotheim, Marcel Dekker, New York, 1986.
2 M. Satoh, K. Kaneto and K. Yoshino, *Technol. Rep. Osaka Univ.*, 1984, **31**, 279.
3 L. A. Paquette, *Principles of Modern Heterocyclic Chemistry*, Benjamin, New York, Amsterdam, 1968.
4 H. Fischer and H. Orth, *Die Chemie des Pyrrols*, band I, Leipzig Academische Verlagsgesellschaft m.B.H., Leipzig, 1934.
5 H. A. Matnishian and S. V. Hakopian, *Arm. Khim. Zh.*, 1978, **31**, 441.