

Synthesis and Characterization of Polyacriflavine

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Keywords: Chemical oxidative polymerization, Coupling reactions, MNDO-PM3, Molecular structure, Morphology, Polyacriflavine, Semiconducting polymer.

Abstract. New functional polymeric, semiconducting materials were synthesized by chemical oxidative polymerization of acriflavine hydrochloride in aqueous solution at room temperature, using ammonium peroxydisulfate as an oxidant. Polymerization products were characterized by gelpermeation chromatography (GPC), FTIR spectroscopy, scanning electron microscopy (SEM) and conductivity measurements. The influence of the oxidant/monomer molar ratio on the molecular structure, molecular weight distribution and the electrical conductivity of polyacriflavines was studied. Molecular weights approach a maximum value of ~20000. The polyacriflavine prepared by using oxidant/monomer molar ratio 1.25 shows the conductivity of 2.8×10^{-7} S cm⁻¹. New substitution pattern shown by FTIR spectroscopic analysis combined with MNDO-PM3 semi-empirical quantum chemical calculations revealed N–C2 coupling reactions as dominant. The formation of phenazine rings in ladder structured polymerization products was suggested from the SEM micrographs.

Introduction

The creation of aromatic diamine polymers by oxidative polymerizations is one of the latest advances in the field of conducting polymers [1]. Aromatic diamine polymers have a lot of novel functions compared with polyaniline and polypyrrole, such as changeable electroactivity, high permselectivity to various electroactive species, unique electrochromism, linear sensitivity of conductivity to moisture, regular variation in conductivity with temperature and external electric field, high sensibilities of the polymer-modified electrode to biosubstances at an extremely low concentration, good detecting ability of electroinactive anions, pronounced electrocatalytic properties, effective absorptivity to heavy metal ions, anticorrosion ability, strong adhesion to metal, and high capacitance.

As a continuation of our recent study devoted to aromatic diamine polymers [2], we have focused our attention on the known fluorescent dye acriflavine hydrochloride, antiseptic agent for skin and mucous membranes, as a promising aromatic diamine monomer. To our best knowledge, as in the case of most of the polymers of aromatic diamines, which have been prepared mainly by electrochemical polymerization [1], there is no report on the chemical oxidative preparation of polyacriflavine. The aim of the present work was to investigate the possibility of acriflavine hydrochloride polymerization in aqueous solution by standard chemical oxidation route, and to study the influence of the oxidant/monomer molar ratio on the molecular-weight distribution, molecular structure and conductivity of obtained novel polymeric materials. Particular attention was

paid to determination of preferential coupling reactions between monomer units by semi-empirical quantum chemical calculations.

Experimental

The monomer, acriflavine hydrochloride (Centrohem, p.a.), representing the mixture of 3,6diamino-10-methylacridinium (acriflavin) and 3,6-diaminoacridine (proflavin) hydrochlorides (Fig. 1), and oxidant, ammonium peroxydisulfate (APS, Centrohem, p.a.), were used without further purification. Chemical oxidative polymerization was performed in aqueous solution at room temperature, using oxidant/monomer molar ratio in the range 1.25 to 2.50.



3,6-diamino-10-methylacridinium chloride hydrochloride



3,6-diaminoacridine dihydrochloride

Fig. 1 Acriflavine and proflavine hydrochlorides.

The samples of polyacriflavine were synthesized by addition of the oxidant solution (5.0, 7.5 or 10.0 mmol of $(NH_4)_2S_2O_8$ dissolved in 10 ml of distilled water) to the monomer solution (4.0 mmol of acriflavine hydrochloride dissolved in 20 ml of distilled water) under stirring. These reaction mixtures were left under stirring at room temperature for 48 h and after this time were filtered. The precipitated dark brown polymer powders were washed three times with 40 ml portions of 0.01 M HCl and dried in vacuo at 60 °C for 3 h.

Molecular weights of polymer samples were assessed with gel permeation chromatography using SH LF-804 column operating with *N*-methyl-2-pyrrolidone and calibrated with polystyrene standards, using toluene as an internal standard. Spectrophotometric detection at a wavelength of 500 nm was carried out. The samples were prepared by dissolving 10 mg of polymeric sample in 5 ml *N*-methyl-2-pyrrolidone containing 100 mg triethanolamine to deprotonate the sample and improve its solubility. Mobile phase, *N*-methyl-2-pyrrolidone, contained 0.5 % LiBr to prevent aggregation. Flow rate was 1 ml min⁻¹. GPC data were treated by CSW 1.7 software.

For conductivity measurements, polymeric samples were pressed into pellets, 10 mm in diameter and 1 mm thick, under a pressure of 124 MPa using a hydraulic pellet press. The conductivity was measured between stainless pistons, at room temperature, by means of an ac bridge (Waynne Kerr Universal Bridge B 224), at a fixed frequency of 1.0 kHz. During the measurement, pressure was maintained at the mentioned value.

Scanning electron micrographs were taken by a JEOL JSM 6460 LV instrument. Powder materials were deposited on an adhesive tape fixed to specimen tabs and then ion sputter coated with gold using a BAL-TEC SCD 005 Sputter Coater.

FTIR spectra of the acriflavine hydrochloride and synthesized polyacriflavines were recorded in the range of 400 - 4000 cm⁻¹ using a MIDAC M 2000 Series Research Laboratory FTIR Spectrometer at 4 cm⁻¹ resolution. Powdered samples were dispersed in KBr and compressed into pellets.

Computational methods

The computational method used here to obtain molecular orbitals, ionization energy (E_i) and the heat of formation (ΔH_f) of individual species is semi-empirical MNDO-PM3 model [3-7] (included in Molecular Orbital Package [8] MOPAC 97, part of the Chem3D Pro 5.0 package, CambridgeSoft Corporation), with full geometry optimization. Input files for semi-empirical computations were the

most stable conformers of investigated molecular structures, with minimized steric energy using MM2 molecular mechanics force-field method [9]. Conductor-like Screening Model (COSMO) technique [10] was used to approximate the effect of a solvent model surrounding the molecule (solvation in water). The restricted Hartree-Fock method (RHF) was used for the molecular structures and the unrestricted Hartree-Fock (UHF) method for radical species.

Results and Discussion

The values of the peak, weight-average and number-average molecular weights, M_p , M_w and M_n , respectively, together with the polydispersity index (M_w/M_n) for prepared polyacriflavines are summarized in Table 1. All synthesized polymers were found to be polydisperse.

Table 1 Summary of the peak, weight-average and number-average molecular weights and polydispersity for different polyacriflavines.



Fig. 2 Molecular weight distribution of polyacriflavine prepared by using APS/monomer ratio 1.88, determined by GPC.

The polydispersity index (PDI) increases with decrease in APS/monomer molar ratio. The PDI have a minimum value of 1.7 for the APS/monomer molar ratio 2.50, and maximum value of 3.2 for the APS/monomer molar ratio 1.25. Bimodal molecular weight distribution (MWD) is observed for polyacriflavine prepared by using the APS/monomer molar ratio 1.88, while other polymeric samples show unimodal MWD. Molecular weight of polyacriflavines approaches a maximum value of ~20000, corresponding to ~70 The low-molecularrepeating units. oligoacriflavines weight (trimers to decamers) were found to be dominant products of acriflavine hydrochloride oxidative polymerization bv using APS/monomer molar ratio 1.25.

In the FTIR spectra of all polymeric samples (Fig. 3), new bands observed at ~1460 and 1506 cm⁻¹, compared with the monomer spectrum, indicate the formation of new aromatic rings in polymerization products: fused pyrazine ring between two acridine rings *i.e.* fused phenazine ring between two quinoline rings. The peak at ~ 1460 cm⁻¹ is attributable to the ring stretching vibration in a newly formed phenazine unit [11,12]. The band at 1506 cm⁻¹ corresponds to the ring stretching vibration (b_{2u}) of phenazine ring, including contribution from the acridine ring stretch (b_l) [11]. Phenazine segment could be formed by oxidation of two N-C2 linked monomer units, followed by intramolecular cyclization reaction, Fig. 4, leading to the ladder segments. In the range 1200-1400 cm⁻¹, where C–N stretching modes appear [13,14], the monomer spectrum shows the bands at 1230, 1254 and 1271 cm⁻¹ while in the spectra of polymerization products only the band at 1265 cm⁻¹ is observed. These changes indicate transformation of primary to secondary and/or tertiary amino group during the polymerization [13,14]. The trisubstituted pattern with one isolated and two adjacent H atoms on fused benzene ring is revealed in the monomer spectrum by the bands at 928 and 858 cm⁻¹, due to aromatic C–H out-of-plane deformation vibrations, γ (C–H), for isolated hydrogen, as well as by the band at 825 cm⁻¹, assigned to the γ (C–H) vibrations of two adjacent hydrogen atoms [13-15]. For polymeric products, the γ (C–H) bands occur at the positions ~ 933 (1H), 854 (1H) (shoulder), and 818 cm⁻¹(2H). Lower intensities and shifting of these bands, compared with corresponding bands of the monomer, indicate transformation of a certain amount of trisubstituted rings to a newly formed tetrasubstituted pattern with two isolated hydrogen atoms (mutually in para-position). The formation of new tetrasubstituted rings is also consistent with

disappearance of the monomer band at 972 cm⁻¹ (C–H in-plane deformation vibration) and the monomer γ (C–H) bands at 775, 764 and 754 cm⁻¹ in the spectra of polyacriflavines [15]. The band corresponding to the N–H⁺ stretching vibration of amine hydrochloride (–NH₃⁺) [13,14] is observed at 3311 cm⁻¹ in the monomer spectrum and at 3319 cm⁻¹ in the spectra of polymeric products synthesized with APS/monomer molar ratio 1.25 and 1.88, while it is not observed for polymeric product prepared with APS/monomer molar ratio of 2.50. This feature is the indication of the lowest content of –NH₃⁺ groups, because of the highest content of ladder segments, in polymeric product prepared with the highest APS/monomer molar ratio of 2.50.



Fig. 3 FTIR spectra of acriflavine hydrochloride and its polymerization products, using APS/monomer molar ratio: 1.25-product 1; 1.88 -product 2; 2.50 -product 3.

Theoretical study of the polymerization mechanism has been based on the MNDO-PM3 semiempirical quantum chemical computations of the heat of formation and ionization energy of acriflavine and proflavine, generated reactive species and reaction intermediates, taking into account solvation effects. Based on the lower ionization energy of hydrated acriflavine and proflavine cation radicals in comparison with parent molecules in aqueous solution, and taking into account increased oxidant power of sulfate radical anion (2.5–3.1 V vs. NHE) [16] in comparison with peroxydisulfate (2.0–2.1 V vs. NHE) [17], we propose generation of the acriflavine and proflavine nitrenium cations in the initiation phase (Fig. 4). Acriflavine and proflavine nitrenium cations further react promptly with the surrounding unoxidized parent molecules, via electrophilic aromatic substitution reaction route, leading in a rate determining step to the formation of the most stable N–C2 coupled dimer intermediates (diacriflavine, diproflavine and acriflavine–proflavine). These intermediates easily release protons forming corresponding N–C2 coupled dimers.



Fig. 4 Acriflavine dimerization mechanism. Two-electron oxidation of the main N–C2 acriflavine dimer followed by intramolecular cyclization and oxidative aromatization is shown.

The electrical conductivity of polymeric products was of the order of $10^{-7}-10^{-9}$ S cm⁻¹ (Table 2). Polyacriflavine sample synthesized by using APS/monomer molar ratio 1.25 has the highest conductivity, 2.8×10^{-7} S cm⁻¹. A number of investigated aromatic diamine polymers show similar

| APS/monomer molar ratio | Conductivity ($S cm^{-1}$) |
|----------------------------|------------------------------|
| 1.25 | $2.8 	imes 10^{-7}$ |
| 1.88 | $4.2 	imes 10^{-8}$ |
| 2.50 | $6.3 	imes 10^{-9}$ |

Table 2 Conductivity data for polyacriflavines.

semiconductivity range [1]. The observed semiconductivity could be explained by the existence of isolated polarons (cation radicals) instead of the known conducting polaronic lattice. The decrease in conductivity with increasing APS/monomer ratio is consistent with the formation of ladder aromatic structures accompanied by disappearance of polaronic sites, via reaction sequence:

 $[-Ar-NH^{\bullet+}-Ar-NH-]_n \rightarrow [-Ar^{\prime}-NH-]_n.$



Fig. 5 SEM images for polyacriflavine sample obtained using molar ratio APS/ monomer = 1.25: a) \times 200, b) \times 1000, c) \times 4000.

The SEM micrographs (Fig. 5) suggested the existence of a certain crystalline structure of the acriflavine polymerization products. Well-defined layers of thickness \sim 0.5–0.8 µm are observed (Fig. 5. c, arrow marked).

Conclusion

FTIR spectroscopic results combined with MNDO-PM3 quantum chemical calculations revealed that the structure of novel semiconducting polymeric materials, obtained by chemical oxidative polymerization of acriflavine hydrochloride with ammonium peroxydisulfate in aqueous solution, contains mainly N–C2 coupled diacriflavine, proflavine and acriflavine–proflavine dimer units. Polyacriflavine contains both ring-opened and ladder segments, obtained by oxidative intramolecular cyclization and aromatization. The content of ladder segments in polymerization product increases with increasing of APS/monomer molar ratio, causing decrease of conductivity.

Acknowledgements

The authors wish to thank the Ministry of Science and Environmental Protection of the Republic of Serbia (Contracts Nos 142047 and 142010) and the Grant Agency of the Academy of Sciences of the Czech Republic (A400500504) for financial support.

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