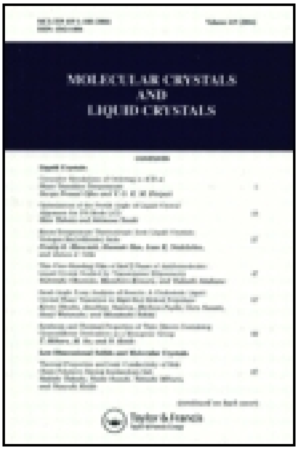

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Structure of Near Order in Conducting Polyaniline Films

O. I. Aksimentyeva [a] & O. I. Konopelnik [b]

[a] Chemical Department of Ivan Franko Lviv National University, Lviv, Ukraine

[b] Physical Department of Ivan Franko Lviv National University, Lviv, Ukraine

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Structure of Near Order in Conducting Polyaniline Films

O. I. Aksimentyeva
Chemical Department of Ivan Franko Lviv National University,
Lviv, Ukraine

O. I. Konopelnik
Physical Department of Ivan Franko Lviv National University,
Lviv, Ukraine

The structure of conducting polymer films of polyaniline (PAN), electrochemically obtained on Pt surface has been studied by means of electron microscopy, electronography and X-ray diffraction analysis. It has been established that in process of conducting film formation two basic structure types of macromolecular arrangement are formed. According to data of electronography at low angles scattering it is found that the polymer film to 80 nm thicknesses is amorphous with a near order in a disposition of structure elements. Follows to photometry of electronographic patterns the radial distribution of intensity as a function of scattering vector $S = 4\pi \sin \theta/\lambda$ *has been obtained. From the disposition of low angle maximum the size of repetitive fragments and a length of the conjugation in which the coplanar orientation of aromatic fragments is reserved (in average 5–6 elemental links) is calculated. With increasing of the film thickness from 80 to 300 nm the content of crystalline phases is arising, but the share of amorphous phase remains enough high. Obtained results permit to be apply for doped polyaniline of the "domain" or "granular" model of conductivity.*

Keywords: amorphous phase; crystalline phases; macromolecular arrangement; polyaniline

INTRODUCTION

Conducting polymers are one of the most interesting classes of low-dimensions (1D) materials. In contrast to conventional semiconductors the charge transport in this systems is realized by nonlinear topological

Address correspondence to O. I. Aksimentyeva, Chemical Department of Ivan Franko Lviv National University, 6 Kyryla-Mefodia St., Lviv, 79005, Ukraine. Tel.: 38-0322-728069, Fax: 38-0322-634009, E-mail: aksimen@org.lviv.net

excitations created in polymer chains as a result of Peierls instability, namely – solutions in trans-polyacetylene, polarons and bipolarons in conjugated polyarenes – poly-*para*-phenylene, polyaniline [1,2] and others. These polymers exhibit a semiconductor property; the reason to that is the existence of the conjugated π-electron bonds. Conjugation of electron system of neighboring elementary link lead to charge delocalization along the polymer chain and possibilities of the charge transport both in one dimension, and in three dimensions over the interchain transitions. The principal particularity of conducting polymers is a drastic anisotropy of their dimension along and across the chain, which leads to existence of specific for polymer oriented state. So conducting polymers with a significant anisotropy of conductivity may be considered as low dimension systems.

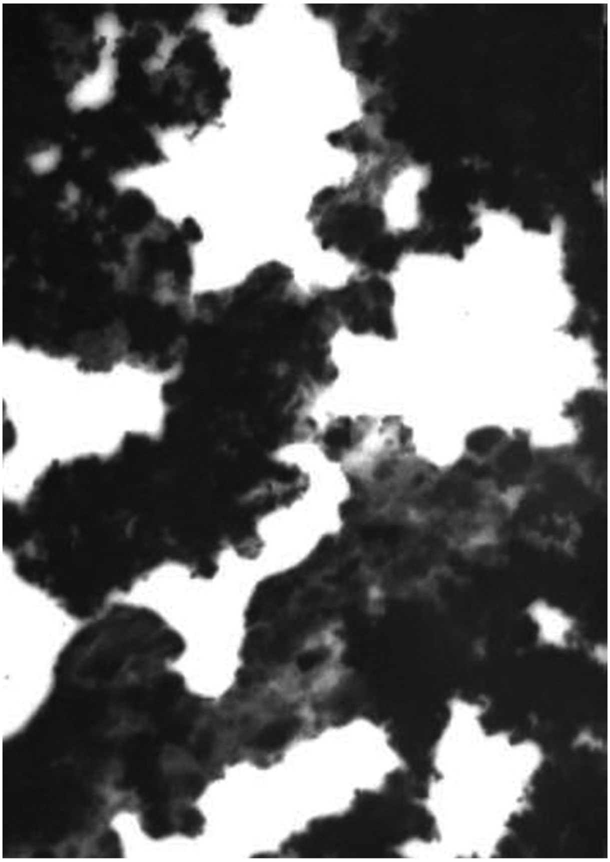
To understanding the mechanism of conductivity it is necessary to know the information on structure of a near order both in volume samples [3] and in a film on the surface of the solid. To find out the role of structure factors in the conductivity in the present work the structure of conducting polyaminoarenes electrochemically obtained on the surface of Pt has been studied.

EXPERIMENTAL

Polymer films were obtained on the plane Pt electrode (area 2,4 cm^2) by electrochemical polymerization of 0,1 M aniline solution in 0,5 M sulfuric acid at current density $i = 0{,}1\text{–}1{,}0\,mA/cm^2$. The structure of the film was investigated by means of transmission electron microscopy (UEMB-100 K), scanning electron microscopy (ISI-DS-130), electronography (EG-100 K) and X-ray diffraction analysis (DRON-2, FeK_α-radiation). To describe a design of polymer in thin layer a statistic method of correlative functions such as radial distribution of atomic density has been used [4]. Following to data of electronography at low angles of scattering and the photometry of electronograph pattern the radial distribution of intensity (I) as a function of scattering vector $S = 4\pi\, sin\ \theta/\lambda$ has been obtained.

RESULTS AND DISCUSSION

With means of transition and scanning electron microscopy it has been established that in process of conducting film formation two basic structure types of macromolecular arrangement are formed – compact amorphous in thin layer and semi-crystalline in thick layers. Thin films before 60–80 nm thickness consist of the ordered islands

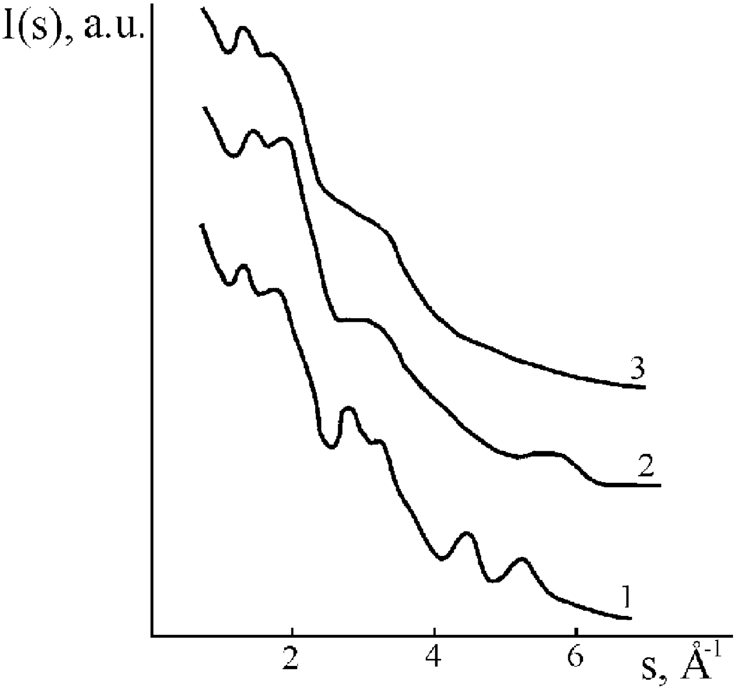


(a)

FIGURE 1 (a) Electronic image of PAN layer on Pt surface (×10000). Film thickness 60 nm; (b) Distribution of scattering intensity for PAN films obtained at current density 0,5 (1); 0,7 (2); 1,0 mA/cm^2 (3). Film thickness 60–80 nm.

(domains) by diameter of 100–1000 nm (Fig. 1). Every domain is assembled of the spherical globules (grains) by 10–30 nm in diameter.

According to data of electronography at low angles of scattering and electron image (Fig. 1) it is found that polymer film before 80 nm thickness is amorphous with a near order in disposition of structure elements. On obtained curves of the radial distribution of intensites for thin polymer films (Fig. 1b) a wide diffusion maximums at $S = 1{,}8\,\mathring{A}^{-1}$, $2{,}9\,\mathring{A}^{-1}$ and an additional low angle maximum at $S = 1{,}35\,\mathring{A}^{-1}$ are observed.



(b)

FIGURE 1 Continued.

From the disposition of low angle maximum the size of repetitive fragments and length of conjugation (25–30 Å) in which the coplanar orientation of aromatic fragments is reserved has been calculated (Table 1).

It is found that morphology of electrochemical synthesized films depends on electrosynthesis conditions, particularly, on electrolysis regime. Following to electron microscopy and electronography the increase of current density leads to structure disordering in polymer layers: on the curves of the distribution of scattering intensity maxima become more indefinite (Fig. 1b).

TABLE 1 Parameters of Near Order Structure for Polyaniline Film (60 nm Thickness)

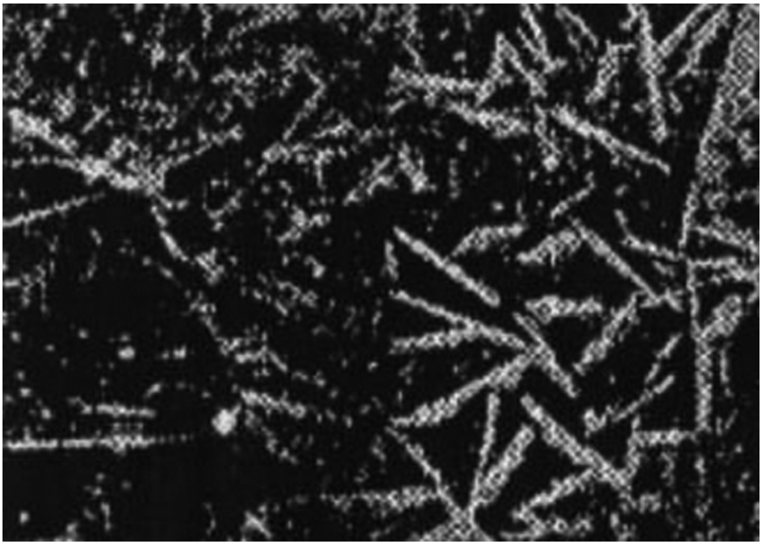
Period of identity, d, Å	Length of conjugation, Å	Number of monomer links
4,6	25–30	5–6

The observation of film grows by electronic microscopy gives the possibility to find, that with increasing of layer thickness from 80 to 3000 nm on the primary formed layer a dendrite crystals by 200–700 nm dimension are growing (Fig. 2a). The content of crystalline phase is arising, but the share of amorphous phase remains enough high.

X-ray diffraction spectra of thick polyaniline films ($l = 3\,\mu\text{m}$) are characterized by assembly of crystalline reflexes (Fig. 2b). A content of crystalline phase (level of crystallinity) increasing in result of polyaniline acid doping and achieves to 41–44% (Table 2). The size of crystallites estimated by Scherrer method [5] also arising with doping in the range of 15–30 nm, which is in a good agreement with the data of electronography (see Table 1).

Calculated from the data of electronography and X-ray diffraction the period of identity $d = 0{,}46$ nm (electronography) and interplane distance $d = 0{,}455$ nm (X-ray analysis) are in a good agreement each other and are clause to the size of Para-substituted phenyl ring (0,453 nm [6]).

Obtained results permit to apply for doped polyaniline the "domain" or "granular" model of conductivity [7–9]. Accordingly to these



(a)

FIGURE 2 (a) Electron image of polyaniline film on Pt surface. Film thickness 3 μm; (b) X-ray powder diffraction spectrum of polyaniline film of 3 μm thickness.

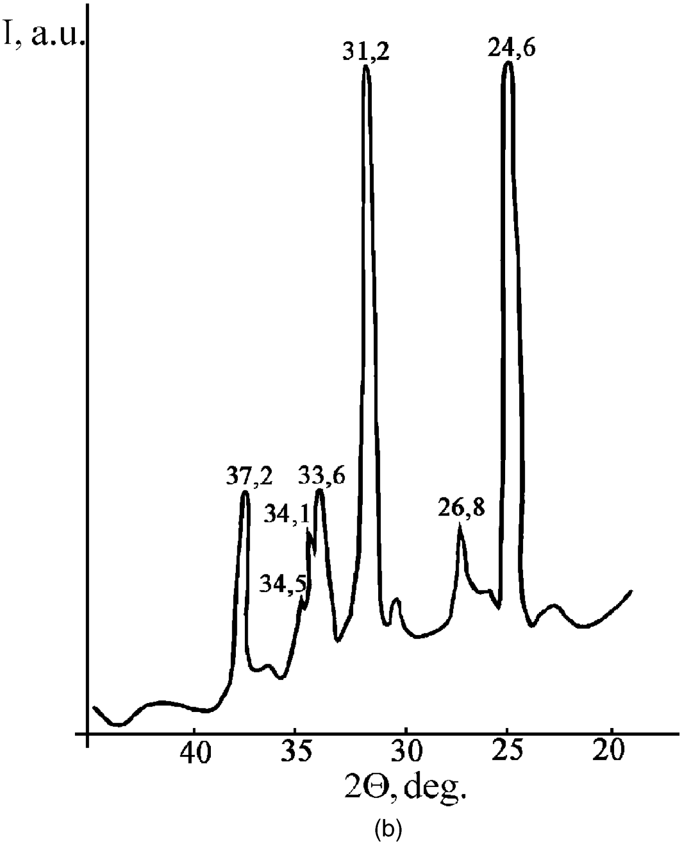


FIGURE 2 Continued.

performances the ordering areas (domain or crystallites) with high conductivity existence in polymer. One polymer chain may be included to some crystallography cells (Fig. 3 [7]). From the experimental electronic image of thin polymer film (Fig. 4) one can observe the existence

TABLE 2 Parameters of X-ray Diffraction, Size of Crystallites and Degree of the Polyaniline Crystallinity

Polymer, doping agent	Interplane distance, d, Å	Crystallite dimension, l ± 10%, Å	Level of crystallinity, I ± 2%
Polyaniline (base)	4,47; 4,23; 3,58	15–20	25
Polyaniline (H_2SO_4)	4,55; 4,37; 3,49	25–30	41
Polyaniline (HCl)	4,66; 4,31; 3,57	20–30	43

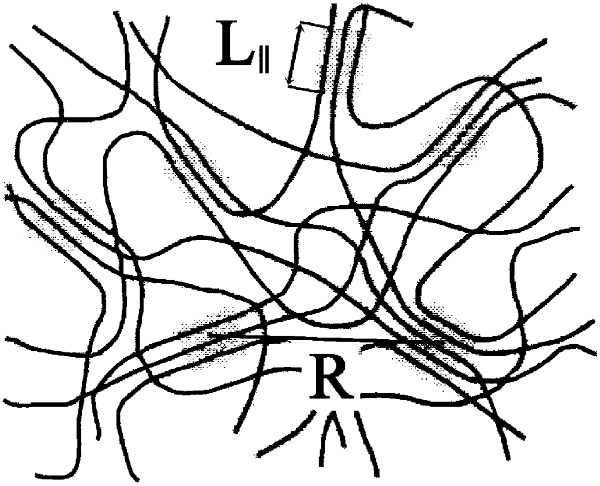


FIGURE 3 Schematic views on the structure of polyaniline. The lines represent polymer chains. The dashed squares mark the regions where polymer chains demonstrate a crystalline order.

of ordered regions, which associate with domain structure of polyaniline film [8].

A charge transport between these domains occurs by hopping mechanism across the low-conductive amorphous shells, which create the energetic barrier to the conductivity. It may be expected that inside crystalline domains the significant interchain overlapping of wave

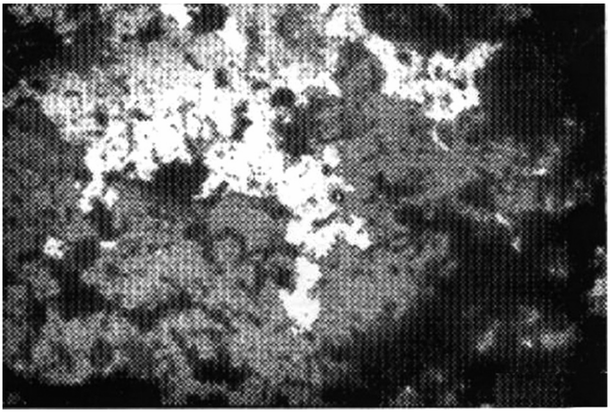


FIGURE 4 Experimental obtained electronic image of polyaniline films on Pt surface. (×8000) Film thickness 80 nm. Size of domains 10–30 nm.

function by all domain volume takes place. In domain the energy levels are quoted, and the size of this quotation is near few eV [7].

In this case a domain may be considered as a metallic grain disseminated into amorphous low conducting matrix on the distance R each other. At the high doping level the tunneling of an electron across the amorphous phase may proceed. To describe the charge transfer in conducting polymers the model of granular metal can be used [7,8].

Electron connections between the metallic domains (well-packet overlapping chain regions) embedded in amorphous media of poor ordered chains: the localization radius of electronic states in metallic grains is of the grain size and is of the scale of polymer repetitive units the amorphous media [7]. It is found [9] that localization length for polyaniline derivatives is (21 ± 6) Å. Interdomain charge transfer may provide by tunneling through resonance states in amorphous region.

CONCLUSION

On the base of radial distribution of intensity as a function of the scattering vector $S = 4\pi \, sin \, \theta/\lambda$ parameters of near order structure of polyaniline have been calculated: the size of repetitive fragments (0,46 nm) and the length of conjugation (2,5–3.0 nm) in which the coplanar orientation of aromatic fragments is reserved. With increasing of the film thickness from 80 to 300 nm, also as in result of acid doping a level of crystallinity achieves to 41–44%. The size of crystallites increases in the range of 15–30 nm. Estimated parameters of near order structure and the localization radius of electronic states in metallic grains are of the grain size and the scale of polymer repetitive units. Obtained results permit to apply for doped polyaniline the “domain” or “granular” model of conductivity.

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