Filament-like structure formation in vacuum thermally evaporated thin films of polyaniline during oxidation in nitric acid

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Oxidation of vacuum thermally evaporated thin films of polyaniline by aqueous nitric acid results in autocatalytic formation of filament-like heterogeneous dissipative structures in the oxidized areas due to non-equlibrium reactions between the reduced form of polyaniline and the oxidant.

Thin films produced by vacuum thermal evaporation of polyaniline (PAN) comprise a structure whose degree of oxidation is several times less than that in the initial form (*ca.* 50%).[1] Hydrolysis of imine fragments of the polymer chain by means of their interaction with strongly bonded water is the most probable cause of this.[1] Considering the whole range of characteristics, the evaporated layers deposited in this way differ dramatically from native emeraldine.[2] This is due to both differences in the degree of oxidation and changes in intermolecular organization. In regeneration processes of the evaporated PAN films (for example, during acid–base cyclic treatment in air), restoration of the initial degree of oxidation and initial three-dimensional intermolecular structure take place.[2–4]

In the present study we have studied the process of regeneration of vacuum thermally evaporated PAN thin films (0.3–0.5 μm) on glass substrates with and without a transparent conducting SnO_2 layer (surface electrical resistivity *ca.* 20 Ohm/□), using aqueous solutions of nitric acid. The vacuum deposited layers were prepared according to the method described in refs. 3 and 4. For the solution preparation nitric acid of ‘chemically pure’ grade and distilled water were used. Treatment of the vacuum deposited layers in 3.3 M aqueous nitric acid was carried out at room temperature after less than one day of storage in a vacuum. During this treatment the changes shown in Figure 1(*a*)–(*e*) were observed. Immediately upon contact of the layer with aqueous nitric acid protonation of the PAN occurs extensively [Figure 1(*a*)]. The higher optical density in the central areas is due to the greater thickness of the film there. Further changes observed are due primarily to the oxidation process and filament-like structure formation in the film [Figure 1(*b*)–(*d*)]. Our earlier spectral investigations[5] showed that colour formation in this system occurs due to the intense growth of a wide absorption band with a maximum at λ *ca.* 800 nm, which is assigned to delocalized polarons.[6] Microscopic examination of the film surface at a hundred-fold magnification in non-polarized light makes it possible to draw conclusions about the rather high homogeneity of the deposited evaporated layer. One may therefore expect the oxidation process to proceed uniformly on the whole area of the film. However, as can be seen in Figure 1(*b*)–(*d*), this is not the case. It should be noted that the uncoloured areas in the vacuum deposited layer are composed of non-oxidized species and the coloured of oxidized ones. Hence, the oxidation process proceeds at different rates in different areas of the film. It is interesting that major, confined areas of oxidation are formed in the early stages, and that the further course of the oxidation process is accompanied by preferential expansion of these oxidized areas. This expansion of the oxidized areas evidently has a fractal character. It should be noted that according to the results of Aoki and coworkers,[7] the oxidation front in a conventional PAN film during electrochemical oxidation also has a fractal character. The results presented here testify to the fact that PAN oxidation is an autocatalytic process. Centres of oxidation formed in the early stages of the process initiate further oxidation in the adjacent areas. The whole film area gradually becomes involved in this process [Figure 1(*e*)]. However, some peculiarities of the process are still not clearly understood. In particular, it is not clear why generation of the oxidized areas proceeds preferentially in the early stage, after which their expansion primarily occurs. This process resembles well-known phase transition processes such as crystallization, condensation, *etc.*[8] As distinct from these phase transitions, in our case the nuclei form filament-like structures. Such a character of the structure formation in PAN during its oxidation is possibly due to the existence of crystallites in the vacuum deposited layer, and the oxidation process is primarily initiated in boundary areas between the crystallites. These phenomena are obviously very interesting, because here we can observe visually for the first time the process of heterogeneous structure formation from an initially homogeneous one, which is essential for reduced PAN. It is generally accepted that it is the heterogeneous structure that is typical, according to the results of various investigation methods, for both PAN and other conducting polymers. The character of this heterogeneity may

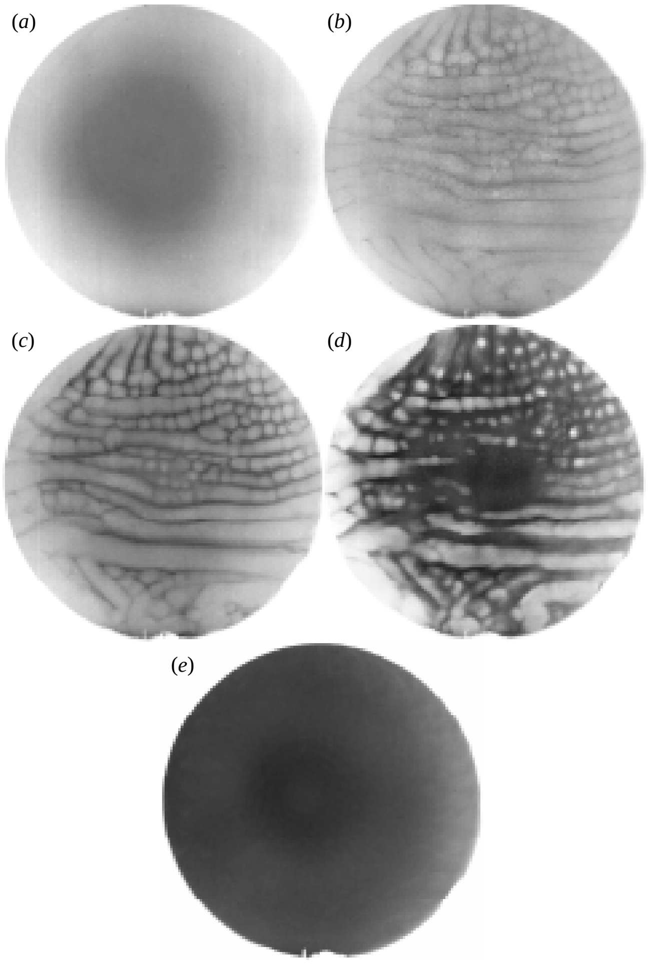

Figure 1 Vacuum evaporated PAN film deposited onto a glass substrate during treatment with aqueous nitric acid; time/s: (*a*) 120, (*b*) 170, (*c*) 190, (*d*) 230, (*e*) 1510.

be due, in particular, to the low value of the percolation threshold for PAN. The results presented apparently testify to the fact that formation of a heterogeneous structure on a macroscopic scale of non-homogeneity is thermodynamically approved under certain non-equilibrium conditions.[9] At the same time, one should account for the fact that, as we have found, if the vacuum evaporated film is deposited onto a transparent conducting substrate, the structural heterogeneities of the above-mentioned scale are not observed under the same oxidation conditions. This is evidently due to a levelling of the electrochemical potential in the PAN layer because of the presence of a conducting SnO_2 layer which participates in the process of electron exchange with PAN. It is possible that the scale of the heterogeneities is essentially less in the latter case and can only be observed by using more sophisticated technical devices.

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