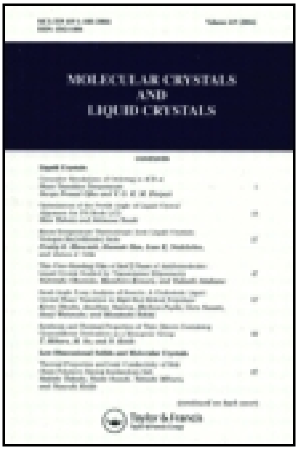

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Sensors Based on Conducting Polyaminoarenes to Control the Animal Food Freshness

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For the visual express-control over animal product freshness, the sensor devices based on conducting polymer films (polyaniline, poly-o-methoxyaniline, and poly-o-toluidine) have been proposed. Sensor action is based on a change in the spectral properties and the corresponding color transitions in conjugate polymer films on the transparent surface at a low partial pressure of ammonia (NH_3) which is evolved at the loss of protein product freshness.

Keywords: ammonia; color change; freshness; optical sensor; polyaminoarenes

INTRODUCTION

In the process of preservation of animal protein food (milk, meat, fish products) under un-satisfactory conditions, a loss of freshness takes place. This process is accompanied by the evolution of gaseous substances such as ammonia, hydrogen sulfide, nitrogen oxides, and others. Among the products of oxidation, ammonia is present always, because the content of nitrogen in all protein molecules is significantly high (up to 15–19%).

For the monitoring of the quality of animal products during their preservation and procession, numerous semiconductor sensors are proposed [1–3]. Organic semiconductors such as molecular crystals and conducting polymers are promising materials for the fabrication of the sensitive elements for gas sensor devices [4–8].

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Optical semiconductor sensors operate without external electric signals, and their optical response can be transferred by fiber-optics communication [7]. However, all the known optical sensors require a special equipment to record the spectral characteristics of sensitive elements under gas absorption and are not suitable for a rapid simple control over the product freshness in refrigerators, markets, etc.

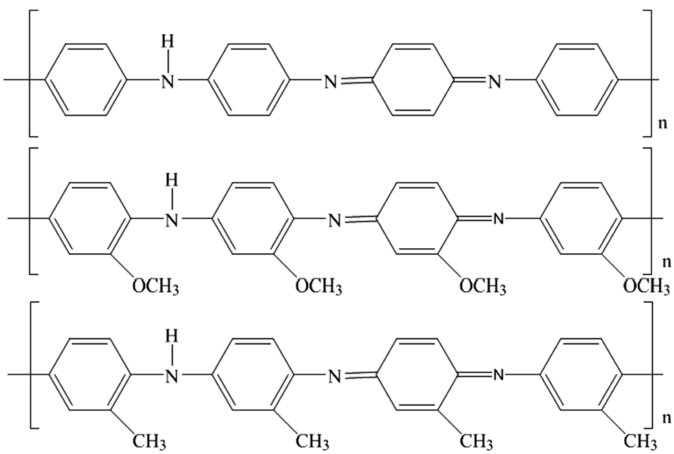
For the express-control over the food freshness in the period of preservation before the use or processing, it is necessary to develop new sensible systems, whose visible changes would be determined at sight, without application of devices to register and analyze input signals. Organic semiconductor sensors based on conjugate polymers meet such requirements [8,9].

The purpose of this work is to develop a device for easy visual indication of the animal products freshness using the color change in sensitive conducting polymer layers.

EXPERIMENTAL

To fabricate a sensitive sensor element, the conducting polymer films of polyaminoarenes (polyaniline, poly-o-methoxyaniline or poly-o-toluidine) have been used. The chemical structure of polymers is shown in Figure 1.

The polymer films were obtained on the surface of glass covered by a conductive SnO_2 layer (surface resistance is 40 Ohm/cm^2) by the



I

II

III

FIGURE 1 Structure of elementary links of polyaminoarenes: I – Polyaniline (PANI), II – Poly-o-methoxyaniline (PoMA), III – Poly-o-toluidine (PoT).

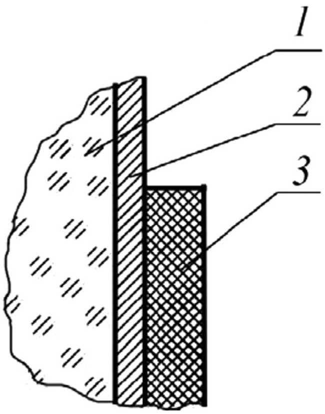


FIGURE 2 Transverse cut of the color indicator of food freshness: 1 – transparent surface, 2 – conducting SnO_2 layer, 3 – sensitive polymer film.

electropolymerization method [9,10]. Electrochemical polymerization was carried out in a 0.1 M monomer solution in the aqueous acid electrolyte at a current density of 0.1 mA/cm^2 during 15 min. This led to the formation a of thin polymer film (300–400 nm in thickness) with bright green color on the electrode surface. After the switching-off of the current source, the electrode with a film was washed by distilled water, dried at a temperature of 60–80°C for 1 h, and cooled in air at room temperature. The construction of the offered indicator [9] is shown in Figure 2.

For monitoring the influence of the ammonia pressure on optical characteristics of the sensor, a sample with polymer film was placed in a quartz hermetic chamber in the working camera of a spectrophotometer SP-46. Air was evacuated to a residual pressure of 10^{-3} Pa by a diffusion pump. A creation of the given pressure of the ammoniac environment was achieved by the supply of ammonia from a bulb. The gas pressure from 10 to 10000 Pa was controlled by a thermocouple vacuum meter. For a very small pressure of ammonia (less than 10 Pa), the saturated vapor of ammonia over aqueous ammonium solutions at various concentrations was employed [11]. The optical absorption spectra of the film under the influence of ammonia were measured in the spectral range 400–1000 nm.

Results and Discussion

It is found that, in the presence of an even small amount of ammonia (a partial pressure of 0.01 Pa), which takes place at the violation of

TABLE 1 Visual Color Changes in the Sensors Used to Control the Animal Food Freshness

	Pressure of ammonia, Pa		
Sensitive polymer layer	0	0.01–0.10	>0.1
Polyaniline	Green	Dark blue	Light blue
Poly-o-metoxyaniline	Green-blue	Violet	Purple
Poly-o-toluidine	Green	Blue-green	Dark blue
Product quality	Fresh	Non-fresh	Damaged

product's freshness, the color of the indicator substances sharply changes—from bright green to dark blue (in the case of PANI and PoT) and from green-dark blue to purple in the case of PoMA. If the freshness of a product gets worse, the evolution of ammonia become more intense, and the film gets light blue or purple color (Table 1).

The color variations in polymer films under the gas action correspond to changes in their optical spectra as shown in Figure 3. The initial as-prepared polymer film in the form of acid-doped emeraldin salt develops a wide band of optical absorption in the interval 700–900 nm. This absorption is caused by polaron–bipolaron transitions in the protonated form of emeraldin and observed also in high

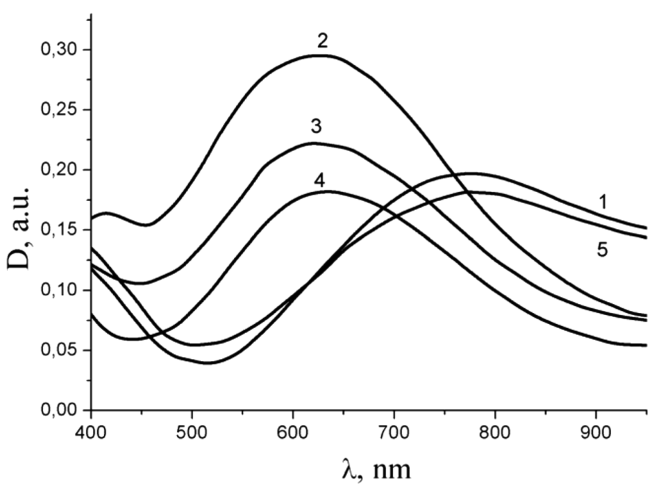


FIGURE 3 Spectral change in the optical absorption of a PANI film at various ammonia pressures, in kPa: 1 – 0; 2 – 0.01; 3 – 2.7; 4 – 5.3; 5 – 0 (after the regeneration of the film in an acid solution).

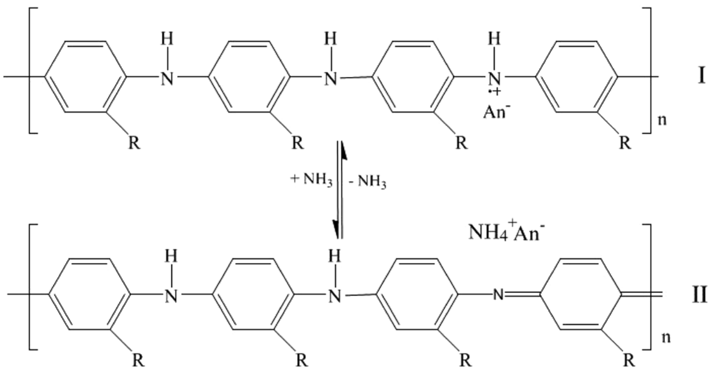


FIGURE 4 Proposed mechanism for the interaction of polyaminoarenes with NH_3 for the protonated emeraldin salt form. R = H (PANI); R = CH_3 (PoT); R = OCH_3 (PoMA).

conductive polyaminoarene films [9,12]. The spectrum undergoes a significant transformation under contact with ammonia molecules (Fig. 3, curves 2–4).

A change in the optical spectra of polyaminoarenes is caused by the interaction of ammonia molecules with the conjugate polymer backbone. The formation of donor-acceptor complexes with nitrogen atoms of the macrochain changes the electron structure of polyaminoarene and leads to a decrease of the *p*-type free carrier's population. Under the influence of a small quantity of the gas, a shape of the optical spectrum of films drastically changes (Fig. 3), and the absorption band in the range 600–650 nm appears. A visual change in the film color is observed. Deprotonation of the polyaminoarene backbone with

TABLE 2 Performances of the Sensor with Different Sensitive Layers

Pressure of ammonia, kP	Performance of sensitive film coloration at different temperatures		
	Polyaniline (t = 18–20°C) (Room conditions)	Poly-o-toluidine (t = 0–1°C) (Refrigerator)	Poly-o-methoxyaniline (t = −5, . . . , −8°C) (Freezer)
1	0.1 s	0.5 s	0.5 s
0.1	0.5 s	1–2 s	2 s
0.01	0.5–1 min	1 min	1 min
0.001	1 min	2–3 min	1–2 min
0.0001	2–3 min	5–6 min	2–3 min
0.00001	5–6 min	8–9 min	7–8 min

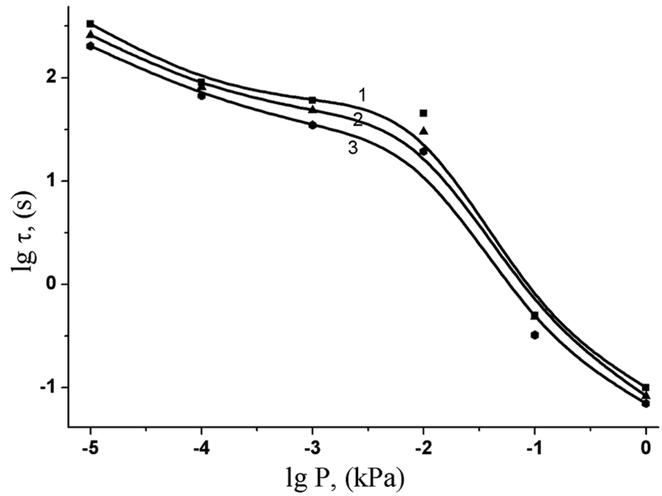


FIGURE 5 Logarithmic dependence of the fast-acting of the sensor on the pressure of ammonia at a temperature of 20°C: 1 – PANI, 2 – PoMA; 3 – PoT.

ammonia leads to the formation of more energetically favorable ammonium ions. The proposed mechanism for the interaction of polyaminoarenes with NH_3 is described by the scheme given in Figure 4. The level of protonation becomes proportional to the pressure of the gas absorbed in the polymer film, which is accompanied by a decrease in the optical absorption (Fig. 3, curves 2–4).

The visual color change of the film is observed instantly after the violation of the food freshness. The action time for the proposed indicators is very small, from 0.1 s to a few minutes, which depends on the nature of an indicator substance, temperature, and partial pressure of the gas (Table 2, Fig. 5).

The advances of the offered indicators consist in a good contrast of color changes, friendliness of the environment, and easy regeneration of the properties, which provides the multiple use and the possibility to obtain an indicator tape directly on (or under) the packing of a commodity.

CONCLUSION

The optical spectra of thin layers of polyaminoarenes on the transparent substrates are sensitive to the pressure of ammonia under its evolution caused by a loss of freshness during the preservation and procession of animal products. The observed effect of a color change depending on the ammonia pressure is used for the fabrication of the sensitive elements of optical sensors used for the visual control over the quality of animal products.

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