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Optical and Electrical Properties of Polyamide Acid and Metal–Polymer Complex Based on Terbium

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Abstract—The basic optical and electrical properties of polyamide acid and its complex with Tb^{+2} have been studied. The occurrence of room-temperature photoluminescence (PL) with an emission peak at 520 nm is established. The activation energy of conductivity at temperatures above 350 K is 2.1 eV. Polyamide acid is comparable in PL intensity with an electroluminescent polymer, poly(*p*-phenylvinylene). © 2003 MAIK “Nauka/Interperiodica”.

Recently, electroluminescence from organic polymers have found increasingly wide and effective application. The best studied electroluminescent materials are polymers with conjugated bonds, poly(*p*-phenylvinylene) (PPV) and its derivatives [1]. Of interest is the search for other polymeric materials possessing a set of properties required for the effective use of these materials in optoelectronics. In particular, of interest are materials for creating hybrid organic–inorganic optoelectronic devices. The promise of this approach has already been demonstrated by examples of luminescence from erbium ions in a polymeric matrix [2] or emission from semiconductor quantum dots incorpo-

rated in an electroluminescent structure based on organic semiconductors [3].

With the above in mind, the study of optical and electrical properties of polyamide acid (PAA) and a metal–polymer complex based on Tb^{+2} (PAA + Tb^{+2}) was undertaken. PAA and (PAA + Tb^{+2}) polymers, polyamide acids with imide and biquinolyl units in their main chain (which are denoted by indices *n* and *m* in Fig. 1), are soluble, hydrolytically stable materials which can be used to obtain transparent films. These films possess good strength and deformational properties and thermal stability at temperatures up to 180°C. The presence of biquinolyl units in the main chain allows

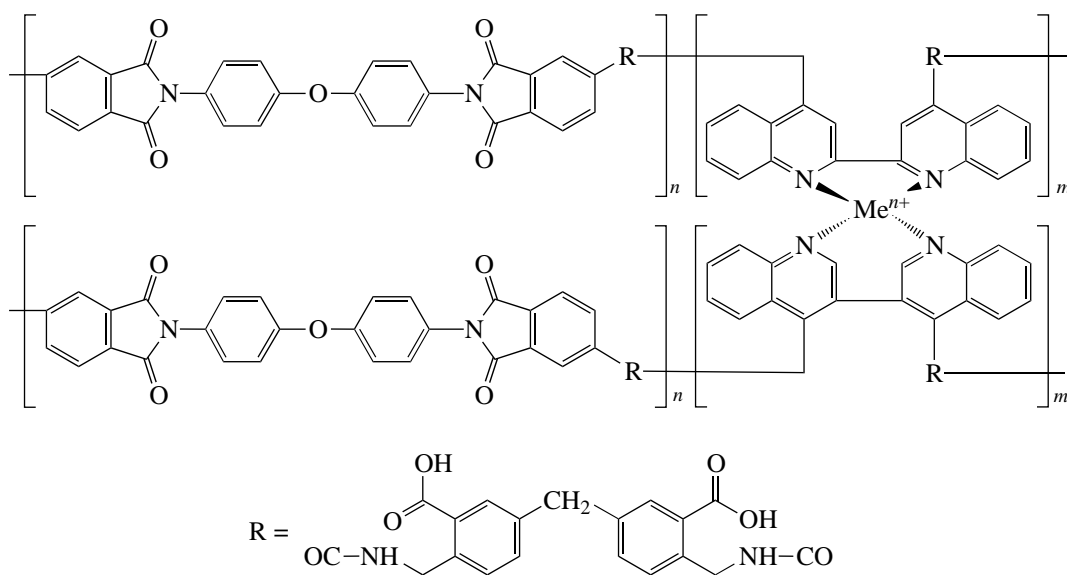


Fig. 1. Structural formula of the metal–polymer complex of polyamide acid.

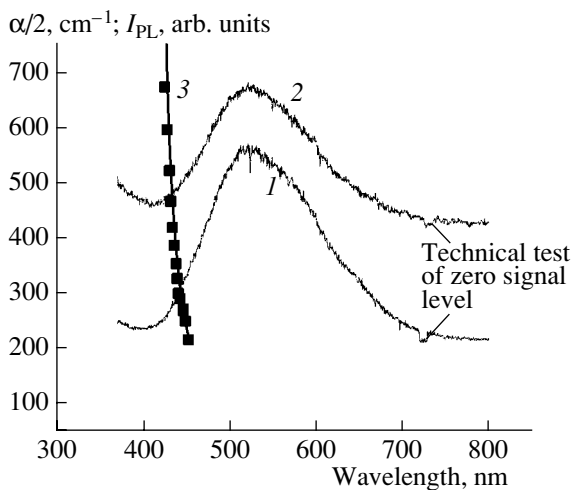


Fig. 2. PL spectra of (1) the terbium complex of polyamide acid (PAA + Tb²⁺) and (2) polyamide acid (PAA), and also (3) the optical absorption spectrum of (PAA + Tb²⁺).

these polymers to form stable soluble complexes with transition metals (general formula is shown in Fig. 1).

The presence of sufficiently long segments with conjugated bonds and the high degree of π -hybridization of orbitals give reason to expect that electrical conduction and effective luminescence will be observed.

On being heated to 180–250°C, the polymers undergo cyclization, being converted into high-strength nonbrittle polybenzoxazinonimides [4]. The polymer solution obtained was used to deposit films by casting on glass substrates, after which the films were subjected to drying at 100°C to constant weight. The thickness of the films was in the range of 20–40 μm .

The following basic electrical and optical characteristics of the material were determined: absorption spectrum in the visible range, PL spectra, electrical conductivity at room temperature, and temperature dependence of conductivity.

The results obtained in studying the optical properties of PAA and (PAA + Tb²⁺) are summarized in Fig. 2. The study of the long-wavelength optical absorption edge demonstrated that the absorption coefficient (α) changes by an order of magnitude, from 10^3 to 10^2 cm^{-1} , in the approximate wavelength range 410–450 nm (curve 3), which corresponds to photon energies of 3 to 2.75 eV. On introduction of terbium, the absorption spectrum of the material shifts noticeably to longer wavelengths.

The PL from PAA and (PA + Tb²⁺) was observed during excitation with 337-nm light. The PL intensity (I_{PL}) was on the same order of magnitude as that for films of the standard photoluminescent material PPV (recorded under identical conditions). The PL spectra, which are peaked at 520 nm (2.4 eV), are shown in Fig. 2. The PL peak positions virtually coincide with the wavelength of the PL peak for PPV. As in the case

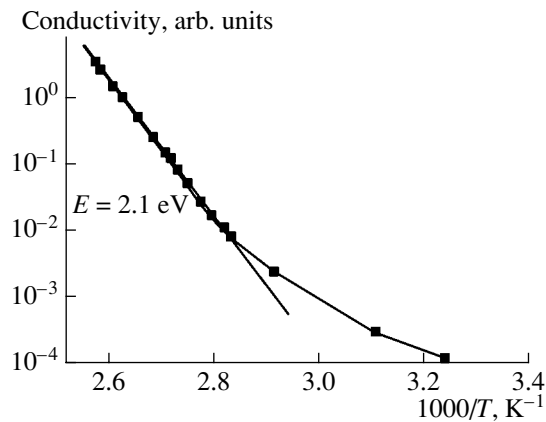


Fig. 3. Temperature dependence of conductivity for the terbium complex of polyamide acid (PAA + Tb²⁺).

of PPV, the luminescence spectrum observed lies at much lower energies than the absorption edge [5, 6]. The metal–polymer complex (PAA + Tb²⁺) shows no characteristic bands of terbium PL. The absence of intrinsic terbium luminescence can be attributed to insufficient electronegativity of the environment of the terbium ion in the metal–polymer complex.

The dark conductivity of PAA and (PAA + Tb²⁺) is low: $\sim 10^{-13}$ $\Omega^{-1} \text{cm}^{-1}$ at room temperature ($T = 300$ K). Figure 3 shows the temperature dependence of the electrical conductivity of this material. It can be seen that the conductivity is characterized by a constant activation energy (~ 2.1 eV) in a wide range of temperatures, from 350 to 400 K.

Since the material used in organic electroluminescent devices is in the form of thin films and a high current density is ensured by carrier injection from the contacts, the relatively low dark conductivity of the material is not an obstacle to its application in optoelectronic devices.

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