Generation of reflected second harmonic and insulator–metal transition in conducting polymer films

O. A. Aktsipetrov
M. V. Lomonosov Moscow State University, 117234, Moscow

V. V. Vereta, L. I. Daĭkhin, and M. D. Levi
A. N. Frumkin Institute of Electrochemistry, Academy of Sciences of the USSR, 117071, Moscow

A. V. Ermushev
Troitsk Innovative Scientific-Research Technological Institute, 142092, Troitsk, Moscow Oblast

A. V. Petukhov
Institute of Crystallography, Academy of Sciences of the USSR, 117333, Moscow

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Second-harmonic generation upon the reflection of light from conducting polymer films has been observed for the first time. Significant changes are found to occur in the nonlinear-optics properties of the films near an insulator–metal transition.

Conducting polymer films are attracting considerable interest because of the sharp changes which occur in their electron conductivity upon doping. Doping increases the electron conductivity of a polymer substantially (by up to 14 orders of magnitude); in the case of polyacetylene, the conductivity can reach values on the order of 10^5 S/cm (Ref. 1). In this letter we are reporting the first *in situ* study of the nonlinear-optics properties of a polyaniline film. The electronic structure, electrical properties, and optical properties of polyaniline have been the subject of active research over the past decade, although the interest in its nonlinear-optics properties is a very recent development.

The method of reflected-second-harmonic generation is winning increasing popularity in research on surfaces and thin films. Second-harmonic generation is sensitive to the adsorption of molecules and ions in submonolayer coverages on surfaces,[2] to

microscopic surface irregularities,[3] and to other characteristics of the surface layer. Second-harmonic generation has been used to study the structure and stacking of the layers in Langmuir films, liquid–crystal films, and other thin films; it has also been used to study the changes in the properties of these films during the application of electrostatic fields and light.[4-6] We have used second-harmonic generation for the first time to study polymer films of aniline in the region of the redox transition of polyaniline from an insulating state (leucoemeraldin) to a conducting state (an emeraldin salt).

The polyaniline film was deposited on a platinum electrode by the technique described in Ref. 7. The second-harmonic generation was observed during the reflection of light at a wavelength of 1064 nm from a pulsed Nd:YAG laser. The pulse length was 10–15 ns, the pulse repetition frequency was 12.5 Hz, and the energy density in a pulse was ~ 25 mJ/cm^2. The system which detected the reflected second harmonic was similar to that described in Ref. 8.

Figure 1 shows the intensity ($I_{2\omega}$) of the second harmonic reflected from a polyaniline film with a thickness of 500–1000 Å as a function of the potential jump (ϕ) at the platinum-electrolyte interface. In the region $\phi < +0.2$ V, the polymer is in a nonconducting state (leucoemeraldin), and the second-harmonic intensity is low. Near $\phi = +0.2$ V, the polymer undergoes a transition to the state of the emeraldin salt, accompanied by the appearance of a hopping electron conductivity.[9] At the same point we observe a sharp increase in the second-harmonic intensity $I_{2\omega}$.

Two factors might be responsible for this effect. In the first place, we know that substantial changes occur in the electronic structure, optical spectrum, and other properties of polymer films near an insulator–metal transition. In particular, these

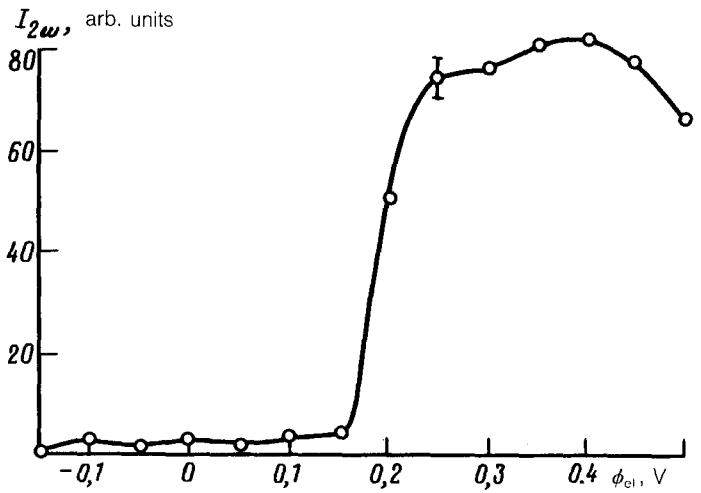

FIG. 1. Intensity ($I_{2\omega}$) of the second harmonic reflected from a polyaniline film as a function of the potential jump (φ) at the platinum–electrolyte interface.

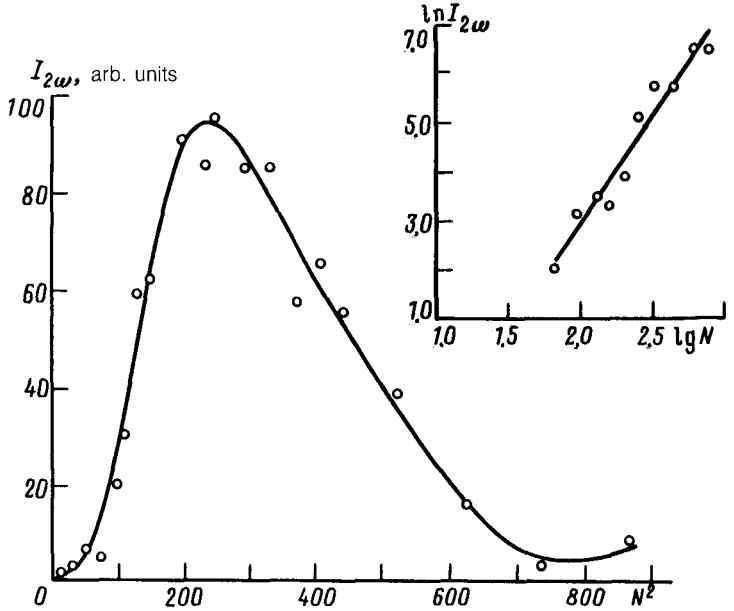

FIG. 2. The intensity $I_{2\omega}$ versus the square of the number of polymerization cycles, N^2. The inset shows $I_{2\omega}(N)$ in logarithmic scale.

films exhibit a very pronounced electrochromism: Color centers appear in these materials in their conducting state and lead to substantial changes in the electron spectrum for the optical range.[10] The appearance of new absorption bands may increase the intensity of the nonlinear-optics response, as the result of a transition of the process of second-harmonic generation into a resonance regime (a manifestation of electrochromism of this sort in nonlinear optics might be called a "nonlinear-optics electrochromism" by analogy with the nonlinear-optics photochromism observed in Ref. 6). Second, the sharp increase in the second-harmonic intensity $I_{2\omega}$ observed near the transition might also be due to a change in the symmetry of the polymer. If the polymer has a structure with an inversion center in its nonconducting state, the second-harmonic generation is due exclusively to quadrupole mechanisms, and the intensity of the second harmonic is low. If the inversion symmetry is disrupted, as it may be in the state of an emeraldin salt, a dipole component of the second-harmonic emission arises and is much stronger than the quadrupole component.

Second-harmonic generation was also studied in films with various thicknesses d. As a polyaniline film is grown by means of cyclic changes in the potential, the film thickness d increases in proportion to the square of the number of cycles, N: $d \propto N^2$ (Ref. 11). Figure 2 shows the N^2 dependence of $I_{2\omega}$ for the case of reflection from the film in its conducting state. At small film thicknesses, $I_{2\omega}$ should be proportional to the square of the film thickness, so we would have $I_{2\omega} \propto N^4$. The inset in Fig. 2 shows $\ln I_{2\omega}$ as a function of $\ln N$ at $N < 15$. A least-squares fit of the experimental results by a linear function yields a value of 3.8 for the slope of the straight line. This value

agrees well with an $I_{2\omega} \propto N^4$ dependence and confirms that the rate at which the film thickness increases itself increases linearly with increasing N. At $N \gtrsim 15$, $I_{2\omega}$ starts to decrease, after going through a maximum. The apparent reasons for the decrease in $I_{2\omega}$ are an absorption in the interior of the film and the centrally symmetric structure of the film, which manifests itself at $N \gtrsim 15$. This change in the symmetry of the growing polymer may be linked with a disorientation of polymer chains as they grow.[12]

In summary, second-harmonic generation upon the reflection of light from a conducting polymer film has been observed for the first time in these experiments. The nonlinear-optics properties of a polyaniline film change significantly near the insulator–metal transition. These changes may be due to either a nonlinear-optics electrochromism or a change in the symmetry of the film. A study of the second-harmonic generation at various thicknesses d of the polyaniline film confirms that the growth rate, $d(N+1) - d(N)$, increases linearly with increasing number of polymerization cycles, N, at $N < 15$. These results show that nonlinear-optics methods can be effective in studying polymer films and synthetic metals.

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