

Self-sensitized Photopolymerization of Pyrrole

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Polypyrrole has been photochemically deposited on different kinds of solid surfaces by illumination with sunlight; this has been interpreted as the consequence of a self-sensitized initiation process.

The search for new conducting materials of a polymeric nature has led to numerous reports, especially dealing with electrochemical growth of such substances.¹⁻³ Recently, two new methods for photo-sensitized polymerization of pyrrole using $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{CuI}(\text{dp})^{2+}$ (**5**) (where bpy = bipyridine and dp = 2,9-diphenyl-1,10-phenanthroline) as sensitizers, have been published.

Herein we report a direct photochemical process in which the pyrrole molecules act as photosensitizers. This simple procedure involves exposing an aqueous solution of pyrrole

deposited onto a solid surface to sunlight. We chose glass, mica, and glass doped with SnO_2 as the substrates for polymerization.

Two types of experiments were performed. The first involved maintaining a HClO_4 (1 M) and pyrrole (0.5 M) suspension in water under atmospheric pressure while irradiating for around 15 h on a glass plate of approximately 3 cm² area. A black polypyrrole film with a metallic lustre of around 100 nm thickness (measured with a Taylor Hobson Talistep) and with a conductivity of around $10^{-3} \Omega^{-1} \text{cm}^{-1}$ was formed.

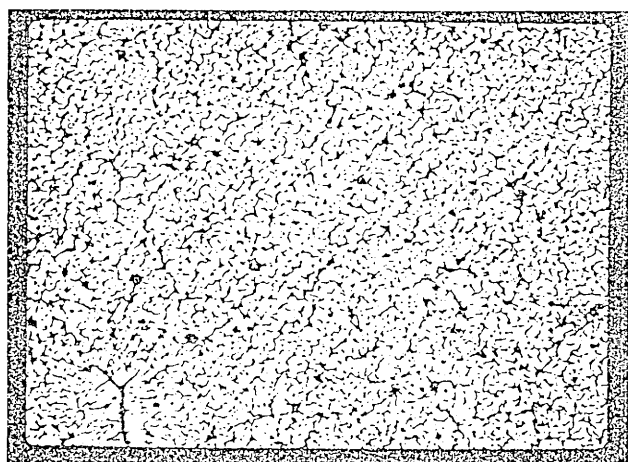


Figure 1

The conductivities were measured by evaporating indium, depositing it in the form of points of a measurable diameter (1–1.5 nm approximately) on the polymer surface and making differential measurements of the resistivities by taking into account the contact resistance between the substrate and the polypyrrole film. A photograph of the microscopic pattern ($\times 50$) is given in Figure 1 showing an almost amorphous pattern which is the result of the polymer growth without any intercalated crystalline zone, as confirmed by X-ray powder diffraction analysis, in which the application of the Debye-Scherrer method leads to apparent amorphous halos.

The second experiment involved two different kinds of solutions in glass tubes into which 3 cm² area (1 \times 3 cm) glass plates were inserted. The tubes were closed with a septum and the solutions were stirred with N₂ by means of two hypodermic needles. Once the solutions were deoxygenated, they were irradiated for a period of around 24 h. The solutions were prepared using Et₄N⁺F₄B⁻ (tetraethylammonium tetrafluoroborate) (0.1 M) and water or acetonitrile as solvents, with pyrrole (0.5 M). The result of the aqueous solution irradiation was the formation of a brown film of 50 nm thickness with a conductivity of around 10⁻⁷ Ω⁻¹ cm⁻¹, which showed two absorption maxima in its UV spectrum (at 1.0 and 3.0 eV approximately). The film was oxidized when it came in contact with atmospheric oxygen, changing colour from brown to black and the conductivity slightly increased.

The deoxygenated solution prepared from acetonitrile gave rise to a very thin polypyrrole film, which showed the same UV spectrum as that prepared from aqueous solution. It seems that polypyrrole formation takes place more slowly from deoxygenated solutions.

In order to explain the process taking place in the deoxygenated solutions, we supposed that the pyrrole monomers absorb sunlight in the near UV region giving rise to photoexcited pyrrole molecules, which are immediately quenched by unexcited pyrrole molecules to give both cation and anion pyrrole radicals.

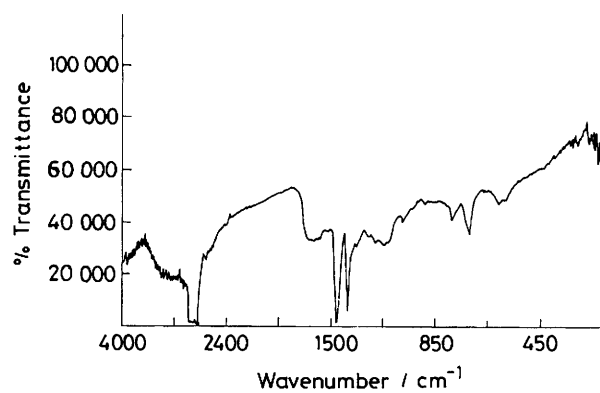


Figure 2

The process involves the following steps.

Step 1 photoexcitation: pyrrole + $h\nu \rightarrow$ (pyrrole)*

Step 2 (pyrrole)* + pyrrole \rightleftharpoons (pyrrole)^{•+} + (pyrrole)^{•-}

Step 3 (pyrrole)^{•+} + pyrrole \rightleftharpoons polypyrrole.

The presence of pyrrole monomers contiguous to both anionic and cationic pyrrole radicals interferes with the back electron transfer, as indicated by step 3. Once an oligomer is formed, light absorption can take place at longer wavelengths so that new radical centres for polymerization appear and the polymerization process continues.

The low values obtained for the conductivity of the polymerized samples indicate that the formed polypyrrole chains do not approximate too much to each other. Another possible reason for the low conductivity is that only a small number of negative dopant molecules are present. Figure 2 shows the IR spectrum obtained for the polypyrrole films. The stretching vibrations of the pyrrole ring are indicated by the bands at 1610, 1510, and 1440 cm⁻¹.

As for the influence of O₂ in the solution, the light-excited pyrrole molecules become oxidized by oxygen giving rise to more rapid formation of cationic radicals and, consequently, rapid formation of polypyrrole film.

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