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Study of the Effect of Adding Aniline on the Polymerization of Pyrrole Aldehyde (Shape and Size of the Resulting Nanoparticles and Film Properties)

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Conducting polymers are important materials with important applications. Most of their applications depend on the shape of the particles and often on their thin films. In this paper, a new copolymer is synthesized from aniline and formylpyrrole in acidic solution. The polymer is described using infrared spectroscopy, and the presence of hexagonal rings in its structure is confirmed. In the scanning electron microscopy (SEM) images, a change in the shape of the particles is observed to become fibres instead of balls in poly(2-formylpyrrole) (PFPy) that confirms the effect of the presence of aniline as a reactant. Thin films are fabricated by anchoring onto glass films of different thicknesses. The surface of the film appears rough and contains many peaks, whose heights range between 10 and 30 nanometers, and the dimensions of its particles match the SEM images.

Провідні полімери є важливими матеріялами з важливими застосуваннями. Більшість їх застосувань залежить від форми частинок і часто від їхніх тонких плівок. У цій статті синтезовано новий кополімер з аніліну та формілпіролу в кислотному розчині. Полімер описано за допомогою інфрачервоної спектроскопії та підтверджено наявність гексагональних кілець у його структурі. На зображеннях сканувальної електронної мікроскопії (СЕМ) спостерігається зміна форми частинок, які перетворюються на волокна замість кульок у полі(2-формілпіролі), що підтверджує вплив присутности аніліну як реаґенту. Тонкі плівки виготовлено шляхом закріплення на скляних плівках різної товщини. Поверхня плівки виглядає шерсткою та містить багато піків, висота яких варіюється від 10 до 30 нанометрів, а розміри її частинок відповідають зображенням СЕМ.

Key words: aniline, 2-formylpyrrole, thin films, polymerization, conducting polymers.

Ключові слова: анілін, 2-формілпірол, тонкі плівки, полімеризація, провідні полімери.

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1. INTRODUCTION

Conducting polymers were discovered in the middle of the last century [1], and have been developed over the past years to obtain materials with unique properties [2]. Conducting polymers are used in the manufacture of sensors and biosensors [3] and electronic applications [4, 5], rechargeable batteries [6], enzyme-immobilization matrices [7], light-emitting diodes [8], optical displays [9], as membranes [10] (in addition to their uses in chemical analysis and others [11]). Thin films are the basis for most applications of sensors, modified electrodes [12], and electrochemical drug release systems all rely on conducting polymer films [13].

Poly(2-formylpyrrole) was prepared by the action of strong acids on the monomer [14]. The resulting polymer particles depend on the method of synthesis and the conditions applied. All the references, which mentioned the preparation of polyformyl, had spherical particles, which agglomerated and formed clusters [14]. Spherical particles are of different sizes and rough surfaces [15]. The particles form thin films easily, and the films have good mechanical properties and good chemical stability [16]. The thickness of polyformylpyrrole thin films can be easily controlled regardless of the supporting substrate [17]. The shape and size of the particles make up the film material greatly affect its properties and, thus, its applications [18].

In this work, we present a method for modifying polyformylpyrrole with a small amount of aniline to improve the linking of polymeric chains and change the shape of the particles and the properties of their thin films.

2. EXPERIMENTAL

2.1. Materials and Measurements

Aniline >98% sigma, Pyrrole-2-carboxaldehyde 98% sigma, Hydrochloric acid 35.5% sigma, Ethanol 99% sigma: polymer was characterized with surface morphologies examined with SEM, EDX and XPS (TESCAN model MIRA3), FT-IR (JASCO FT/IR model M4100) spectrophotometer between 4000 and 400 cm^{-1}, and AFM (Nanosurf model: eseyscan2).

2.2. Polymer Synthesis

2-Formylpyrrole (20 mmol) was dissolved in 25 ml of alcohol (5% hydrochloric acid prepared by adding the appropriate amount of concentrated 35% hydrochloric acid to the alcohol). Then, aniline is added in a varying percentage each time to the reaction medium. The mixture is stirred, and a bright yellow precipitate is formed.

Then, it soon begins to dissolve and the solution becomes darker and darker until a very soft dark green precipitate is formed. After a period of 48 hours, the precipitate is separated with the sediment and washed well several times with distilled water and then alcohol.

2.3. Films Fabrication

Films fabricated by anchoring method with glass plates were immersed in the reaction medium (four sheets in each experiment) and removed successively for different times. The films were gently washed with distilled water and alcohol, then, dried with gentle air without touching the film and prepared for later study. Table 1 shows a list of the experiments carried out and the weight yield of the reaction. The thicknesses of thin films were calculated from the optical absorption spectrum [17].

3. RESULTS AND DISCUSSION; POLYMER CHARACTERIZATION

Scanning Electron Microscope Images (SEM). SEM images provide important information about the physical size, shape, surface nature, and accumulation method of nanoparticles in a descriptive manner. Figure 1 shows SEM images of the prepared samples. We note that the polymer has particles in the form of fibres with sharp irregular angles. The fibre sizes are for diameter: 95, 75, 123, 156 nm and for length: 800, 1200, 1500, 1800 nm for the percentage of aniline of 2, 5, 10, 15%, respectively. In comparison with the SEM images of the same polymer prepared in the absence of aniline, we notice a significant difference in the shape and size of the prepared particles, as the prepared particles appear spherical in shape, while they are in the form of fibres and rods, if they are prepared in the presence of aniline.

FT-IR Spectrum. Figure 2 shows the FT-IR spectrum of the resulting polymers. In the IR spectrum, a broad peak around 3500 cm^{-1} is due to the stretching of the [O–H] bond, and this band obscures completely any peak of the primary or secondary amine. A weak peak at 1730 cm^{-1} is due to stretching of the unreacted carbonyl group at the end of the polymer chain. The peaks at 1585, 1490,

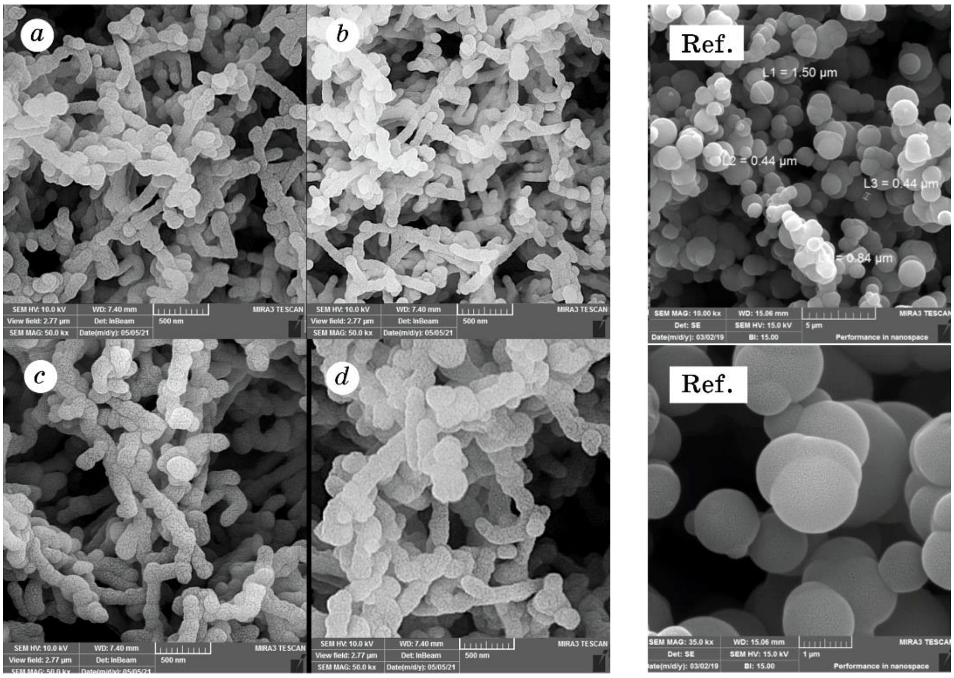

Fig. 1. SEM images of the polymer with percentage of aniline: (*a*) 2%; (*b*) 5%; (*c*) 10%; (*d*) 15%; and (Ref.)—reference [14].

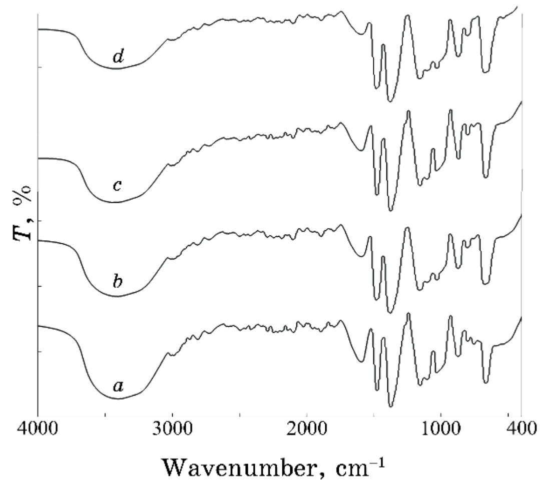

Fig. 2. The FT-IR spectrum of the resulting polymers.

1290 and 1160 cm^{-1} mostly belong to the hexagonal rings that confirms the inclusion of aniline within the polymer chains.

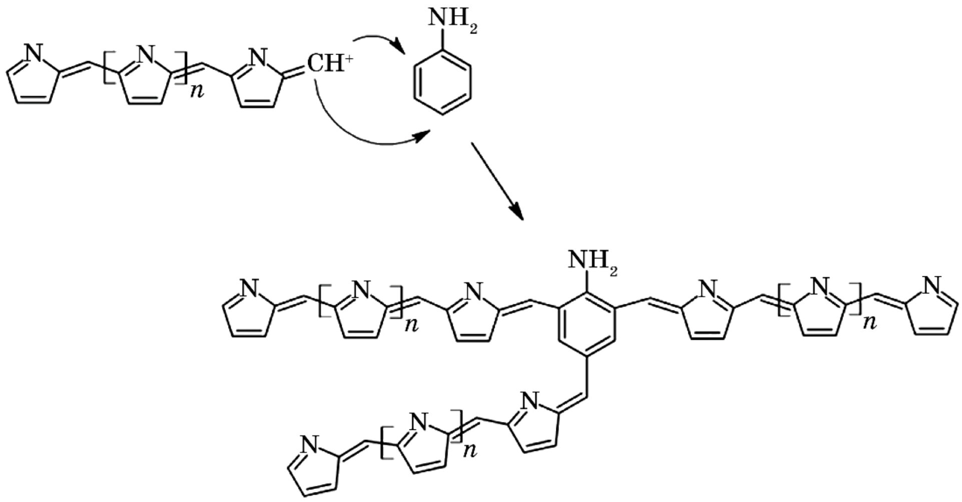

Fig. 3. Proposed linking scheme for polymeric chain.

An increase in the percentage of aniline in the reaction solution corresponds to an increase in the intensity of signals returning to the hexagonal rings compared to others.

During the experiment, a yellow precipitate formed at the beginning of the experiment and then dissolved again later. The precipitate is Schiff's base, which dissociates in acidic media into the aldehyde and amine. The presence of the active aromatic ring in aniline during the reaction makes it vulnerable to electrophilic attack by the electrophile formed during the polymerization reaction, and this helps to link the polymeric chains and form random branched chains. Figure 3 shows the proposed linking scheme for polymeric chains.

On the other hand, the presence of the amine in the acidic environment gives aryl ammonium salts, which may play the role of an electrophile that attacks the active aromatic rings (both aniline and pyrrole) in the presence of an oxidizer (here, the aldehyde plays the role of the oxidizer), which gives possibilities for different binding to the polymer structure as is published in Ref. [19].

Figure 4 shows the proposed possibilities for the structure of polymers formed during the reaction. The polymer formed is a mixture of all possibilities, and one cannot be preferred over the other.

Thin Films. Five thin films with different thicknesses were fabricated during the reactions for different reaction times. Table shows the reaction times and film thicknesses. The thickness of the films increases with increasing reaction time in an unsteady manner, and this is consistent with that researchers have found in previous studies [17]. The thickness of the first films (with different durations)

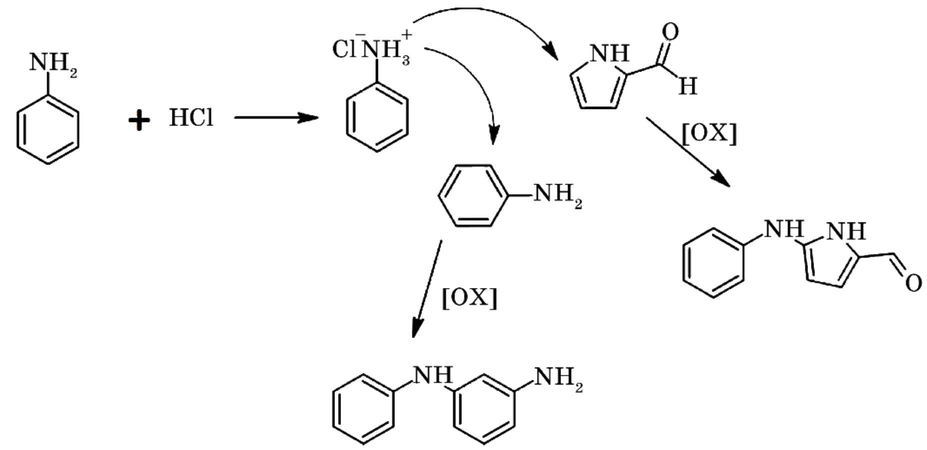

Fig. 4. The proposed possibilities for the structure of polymers formed during the reaction.

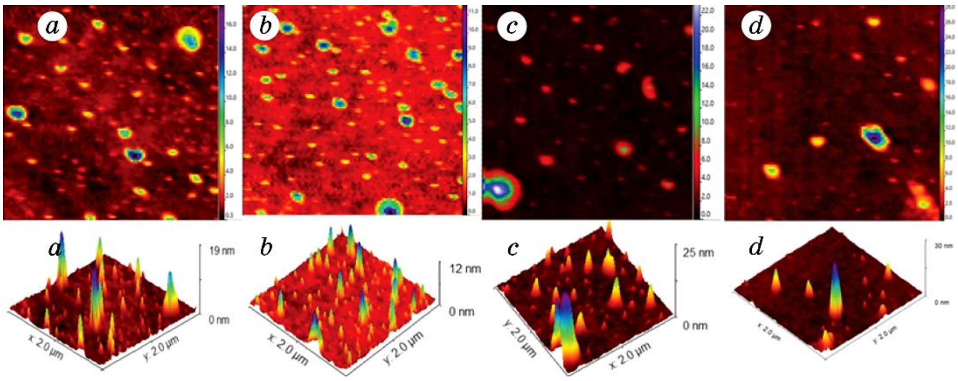

Fig. 5. AFM images of thin films on glass (3*D* image and topography at 6 h).

also increases with the decrease in the percentage of aniline due to the consumption of part of the aldehyde in the form of Schiff's base at the beginning of the reaction. In addition, the movement of the precipitate, when the reaction is triggered, reduces the stability of the molecules attached to the surface of the substrate during the beginning of the reaction. For long times (> 2 h), the films thickness are increase with increasing percentage of aniline. It is believed that this is due to the activity of the aniline ring in the reaction.

Figure 5 shows AFM images of thin films on glass. The surface of the film appears rough and contains many peaks, whose heights range between 10 and 30 nanometers, and the dimensions of its particles match the SEM images.

4. CONCLUSIONS

Adding aniline to the 2-formylpyrrole, polymerization reaction affects the shape and size of the polymer particles, giving rod-shaped particles of different sizes instead of balls. Aniline causes changes in the positioning and shape of the particles, which make up the prepared thin films. Aniline enters the polymer chain in two ways. The first one is by linking the chains as a result of the electrophilic addition to the aromatic ring, and the second one is as a result of the formation of an alkyl ammonium that plays the role of an electrophile in the presence of the aldehyde as an oxidant. This leads to the formation of a random copolymer of aniline and 2-formylpyrrole.

HIGHLIGHTER

1) Changing the shape of the polyformylpyrrole particles by adding a small amount of aniline.
2) Formation of a random copolymer of aniline and 2-formylpyrrole with properties different from the base polymer.
3) Thin films of different thicknesses are easily fabricated using the anchoring method.

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