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Simultaneous Polymerization-dyeing for Helical Vessels via Oxidative Coupling with Bach Reaction

Polymer Dyeing

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ABSTRACT

Azo dyes are essential to our lives and are synthesized by coupling reactions. In this research, we carried out dyeing of helical vessels with an azo polymer. The polymer thus synthesized in this study was characterized with infrared absorption and UV-vis absorption spectroscopy measurement. We observed the surface structure of the helical vessels coated with the azo polymer with optical microscopy and scanning electron microscopy (SEM).

Keywords: azo polymer, dye, oxidative coupling

Introduction

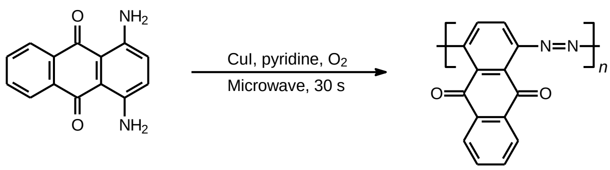
The first chemical coloring material found in the world is mauve or aniline-purple. It was discovered in the process of synthesis of quinine, an antimalarial drug by Perkin in 1856[1]. The first azo dye was synthesized by Griess after two years of the synthesis of the aniline-purple[2,3]. Many chemically synthetic dyes have been produced since development of the artificial dyes[3]. Further, various types of pigments have been developed until now. For instance, pigments for textiles, papers, food and so on[4–7].

Azo compounds are one of the most representative chemically synthetic dyes, and many kinds of them are used for textiles industry [8,9], such as naphthol dye[10–12], orange (II)[4,13,14], methyl red and so on[15,16]. They are essential to our daily lives in modern textile industry. Generally azo dyes are synthesized by coupling reactions with amino groups[17–19].

Oxidative coupling polymerization was carried out by Bach et al. in 1960s as one of the methods for synthesis of azo dyes. Oxygen was used as an oxidizer in the polymerization reaction. The report showed that many types of azo dye polymers including polyazobenzene, polymer with peptide bonds were synthesized. Color of azo polymers in the report were black, brown and red-brown[20].

In this research, we aimed to synthesize azo polymer with oxidative coupling reaction previously carried out by H. C. Bach et al. ca. 50 years ago (Bach reaction). We carried out the oxidative coupling azo-polymerization in the presence of helical vessels of plants. This process allows performing simultaneous polymerization-dyeing for the natural cellulose forming helical structure.

Experimental



Mono1 Poly1

Scheme 1. Synthesis of poly1.

Into a flask were added cupper iodine (547 mg, 2.87 mmol), 1,4-diaminoanthraquinone (2.507 g, 10.5 mmol) and pyridine (30 mL). After stirring and bubbling with oxygen for 1 h at room temperature, helical vessels were added to the solution and the mixture was heated by microwave for ca. 30 s. The helical vessels we employed in this study were collected from leaves of cabbage. Then, helical vessels were separated from the mixture and added to excess amount of methanol. The helical vessels thus obtained were well dyed by the polymer.

Results and discussion

Infrared spectra

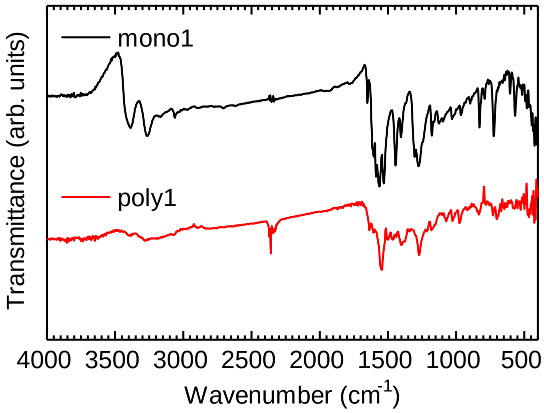


Figure 1. Infrared absorption spectra for mono1 and poly1.

Infrared absorption spectra for mono1 and poly1 are shown in Figure 1. The N-H stretching vibration is observable at 3267 cm^{-1} for mono1. Poly1 shows no signal at 3267 cm^{-1}. On the other hand, weak N=N stretching vibration is observable at 1467 cm^{-1}. The C=O stretch vibration is observed at 1548 cm^{-1}. The Ar-H stretching vibration appears at 1402 cm^{-1}. The absorption at 1271 cm^{-1} is due to Ar stretching vibration This result indicates that the oxidative polymerization was successfully achieved.

Optical microscopy and scanning electron microscopy (SEM)

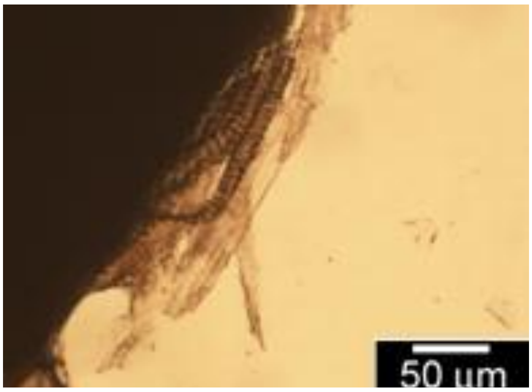


Figure 2. Optical microscopy image of helical vessels after dyed.

An optical microscopy image of the helical vessels coated by poly1 is displayed in Figure 2. Coloration of the helical vessels by poly1 is visually observed.

The scaning electron microscopy (SEM) images are shown in Figure 3, comfirming maintanence of original structure after polymer dyeing.

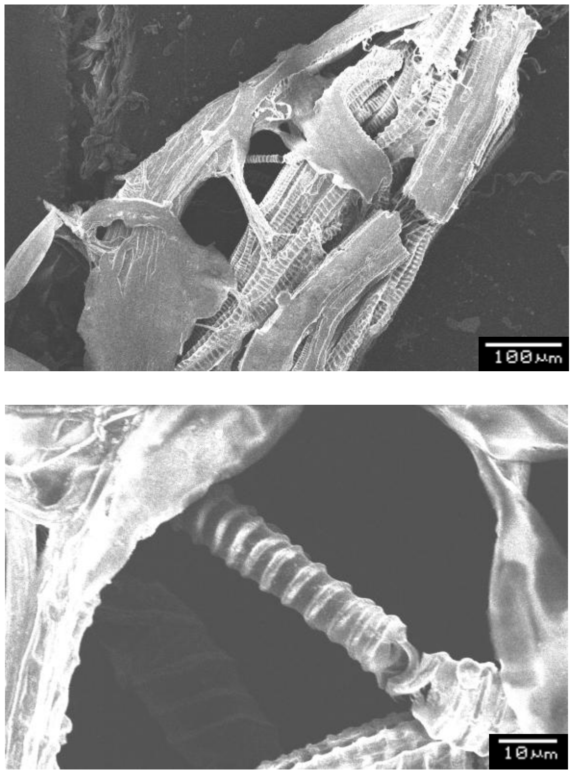


Figure 3. SEM images of helical vessels dyed by poly1. a) Entire image of the polymerization-dyeing helical vessels. Magnification image of the helical vessel coated by the azo-polymer (poly1). Maintaining after polymerization-dyeing can be confirmed.

UV-vis absorption spectrum

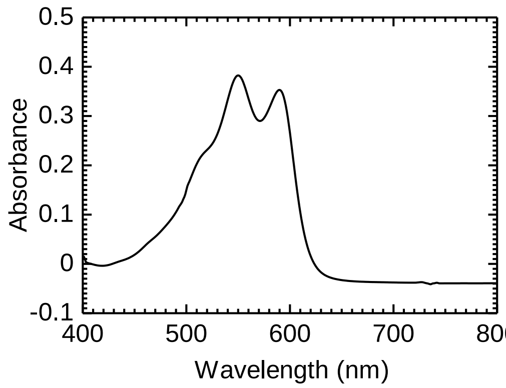


Figure 4. UV-vis absorption spectrum of poly1 in tetrahydrofuran (THF) solution.

UV-vis absorption spectrum of the polymer was obtained in dilute solution of tetrahydrofuran (THF). The UV-vis absorption shows that poly1 shows absorption bands at 550 nm and 590 nm. The absorptions are due to π-π* transition of dibenzoquinone and n-π* transition of azo group in the main chain.

Conclusions

Synthesis of azo polymer with oxidative coupling was succeeded. Helical vessels were dyed in the process of polymerization for synthesis of the azo polymer with adsorption. The helical form of the micro-vessels is maintained after "the simultaneous polymerization dyeing".

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