

Electrochemical polymerization of pyrrole in supercritical carbon dioxide-in-water emulsion

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Abstract

Supercritical carbon dioxide is an environmentally benign solvent but its low polarity limits electrochemical reactions in it. We now report the electrochemical polymerization of pyrrole in a supercritical carbon dioxide-in-water (C/W) emulsion in the presence of a surfactant. Black polypyrrole films were formed on Pt electrodes, whose conductivity was comparable with non-oriented polypyrrole prepared in conventional solvents. The structure of the polypyrrole films was confirmed by IR and Raman spectroscopic measurements. *p*-Toluenesulfonic acid was a suitable supporting electrolyte among the electrolytes examined for the electrochemical polymerization in the C/W emulsion. A typical nodular morphology was observed on the basis of the SEM and AFM measurements. Confocal scanning microscope revealed the formation of a fine uneven texture on the film prepared in the C/W emulsion.

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Keywords: Supercritical carbon dioxide; Electrochemical polymerization; Polypyrrole

1. Introduction

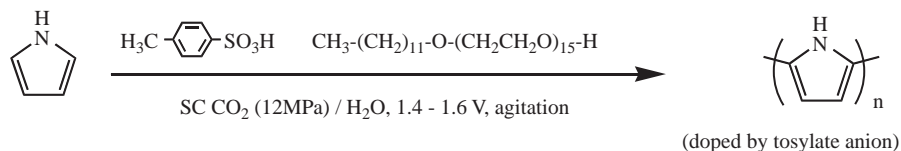
Dense carbon dioxide is one of the promising reaction media alternatives to harmful organic solvents. In addition to its mild critical conditions ($T_c = 31\text{ }^\circ\text{C}$, $P_c = 7.4\text{ MPa}$), carbon dioxide is a non-flammable, virtually inert, and non-toxic solvent. It has been reported that many organic reactions can be carried out in dense carbon dioxide as an inert medium [1–5]. Although supercritical carbon dioxide is a poor solvent for most high-molecular-weight polymers, successful homogeneous or heterogeneous radical polymerizations have been achieved in it since 1992 [6–15]. Metal-catalyzed polymerizations, such as cationic polymerization, metathesis polymerization and oxidative polymerization, have also been reported in the literature [16–20]. Although most of the successful polymerizations are targeted to vinyl polymers, there are a few reports for the preparation of condensation polymers using

supercritical carbon dioxide. DeSimone and coworkers reported the melt polycondensation of a nylon salt to form aliphatic polyamides [21] and a transesterification using a supercritical fluid extraction technique to form polyesters or polycarbonates [22,23].

In 1997, Armes and co-workers reported the preparation of polypyrrole through chemical oxidative polymerization as the first example of the preparation of a conductive polymer in supercritical fluids [24]. The conductivity of the polypyrrole prepared using $\text{Fe}(\text{CF}_3\text{SO}_3)_3$ was two to three orders of magnitude lower than those of the polypyrrole prepared in conventional solvents. Conductive composites were also prepared through the in situ polymerization of pyrrole or thiophenes via chemical oxidative polymerization [25,26]. Electrochemical polymerization is an alternative method to prepare conductive polymers, which is especially useful for the preparation of thin films. However, it is widely recognized that dense carbon dioxide is a non-polar solvent and is not suitable as a medium for electrochemical reactions [27–29]. The addition of a co-solvent or a modifier is one solution to overcome the limited solvent polarity. Tokuda reported the electrochemical synthesis of aromatic carboxylic acids in supercritical carbon dioxide in the presence of DMF or

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Scheme 1.

acetonitrile as a co-solvent [30]. Mabrouk and co-workers reported the electrochemical polymerization of pyrrole in supercritical carbon dioxide with acetonitrile as a modifier [31]. The other solution for the low solvent polarity is the addition of a surfactant to form an emulsion of supercritical carbon dioxide and water. Both water-in-CO₂ and CO₂-in-water emulsions with the addition of surfactants have been reported in the literature [32–35]. In particular, a continuous water phase in the CO₂-in-water (C/W) emulsion allows an electrochemical reaction in the emulsion.

Recently, Yoshida et al. reported nickel electroplating in the emulsion of supercritical carbon dioxide and an electrolyte solution in the presence of a surfactant [36,37]. Uniform nickel films with a smaller grain size and increased hardness were obtained by the electroplating reaction although the reason for the formation of the high quality films was not experimentally identified. Since carbon dioxide is miscible with gaseous byproducts, which could be formed during the electrochemical reactions in water, the electrode surface could be cleaned and striped during the electroplating in the C/W emulsion, which presumably contributes the formation of the homogeneous nickel films.

In this paper, we report the electrochemical polymerization of pyrrole in a supercritical carbon dioxide-in-water emulsion in the presence of a surfactant (Scheme 1). In addition to providing a new polymerization system using supercritical carbon dioxide without any organic solvents, the C/W emulsion as a unique reaction medium may influence the properties and morphology of the resulting polypyrrole films. The resulting films were characterized by spectroscopic and microscopic measurements in order to elucidate the effect of the dense carbon dioxide on the formation and morphology of the polypyrrole films. Macroscopically homogeneous, but rough films were unexpectedly obtained by the electrochemical polymerization in the C/W emulsion.

2. Experimental section

2.1. Materials

Pyrrole (Kanto Chemical Co., Inc., Tokyo, Japan) was purified by distillation before use. A commercially available *p*-toluenesulfonic acid monohydrate (Tokyo Kasei Co., Ltd, Tokyo, Japan) was used without purification. Sodium dodecylbenzenesulfonate and sodium *p*-toluenesulfonate were purchased from Kanto Chemical Co., Inc. and used without further purification. Anhydrous lithium tetrafluoroborate (Acros Organics) was used without purification. Poly(oxyethylene)

lauryl ether (C₁₂H₂₅(OCH₂CH₂)₁₅OH) (solution (25%) in water, HLB = 14) was a kind gift from Toshin Yuka Kogyo Inc., Tokyo, Japan and was used for the polymerization without purification. The neat poly(oxyethylene) lauryl ether was obtained by drying the extract from its NaCl aqueous solution (10%) with chloroform in vacuo at 50 °C for 12 h. De-ionized water was used for the electrochemical polymerizations. The platinum plate was purchased from Nilaco Co., Ltd, Tokyo, Japan (thickness: 0.3 mm) or Tanaka Kikinokogyo K.K., Tokyo, Japan (thickness: 0.7 mm). Each platinum plate was cut to a rectangular piece (1 cm × 2 cm) for use as an electrode. Thick platinum electrodes were used for the morphology investigation and thin electrodes were used for all other experiments.

2.2. High pressure equipment

The high-pressure reactor used for the electrochemical polymerization is shown in Fig. 1. A commercially available reactor (JASCO EV-3, pressure rating: 35 MPa) was modified for the purpose of electrochemical reactions under high pressure. The total volume of the reactor was ca. 50 mL. A safety bulb, whose open pressure was set to 30 MPa, was connected to the reactor to minimize any accidental pressure increase. Platinum wire insulated to the reactor by a PEEK tube was attached to the platinum electrodes and the electrodes were placed at a distance of 2 cm. A visible high-pressure view cell equipped with sapphire windows (pressure rating: 34.3 MPa)

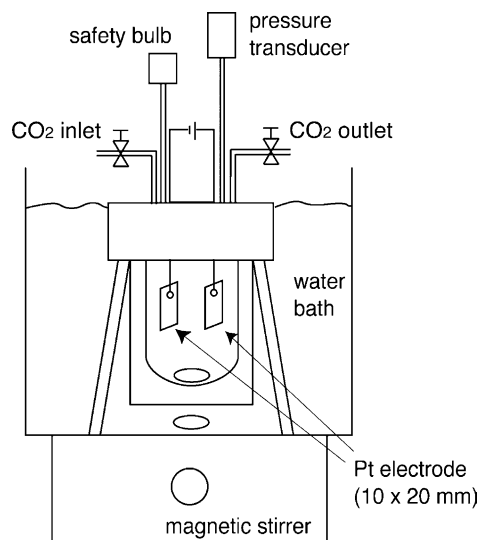


Fig. 1. High pressure reactor and reaction setting of the electrochemical polymerization in the C/W emulsion.

was purchased from Taiatsu-Glass Kogyo Inc., Tokyo Japan. The cell was made from Hastelloy and the total volume of the cell was ca. 20 mL.

2.3. Monitoring of emulsion formation

The formation of a supercritical carbon dioxide-in-water emulsion was visually monitored using the high-pressure view cell. De-ionized water (15 mL) and octa(ethyleneoxide) monododecyl ether (0.45 mL, 3 vol%) were first charged into the high-pressure view cell. The cell was immersed in a water bath (35 °C), then carbon dioxide was introduced into the cell by an HPLC pump (JASCO SCF-Get) to 12 MPa. After 30 min, the solution was stirred using a magnetic stirrer (1100 rpm). The formation of the emulsion was visually monitored through the sapphire windows of the view cell.

2.4. Solubility test

Solubility testing of the chemicals in the supercritical carbon dioxide was carried out using the high-pressure view cell. A small amount of the sample (typically 50 mg or 100 µL) was charged into the view cell. The view cell was immersed in a water bath (35 °C), then carbon dioxide was introduced into the cell to 12 MPa. After 30 min, the CO₂ phase was stirred using a magnetic stirrer (1100 rpm). The solubility of the sample was qualitatively determined through the sapphire windows of the view cell.

2.5. Electrochemical polymerization

The electrochemical polymerization of pyrrole (0.1 mol/L) in the C/W emulsion was carried out in the presence of the surfactant (3% (v/v)) and a supporting electrolyte (0.1 or 0.5 mol/L). A typical experimental procedure is described as follows. *p*-Toluenesulfonic acid monohydrate (2.85 g, 0.015 mol) was dissolved in water (30 mL) and the solution was sonicated for 15 min, then bubbled with nitrogen in order to exclude any oxygen dissolved in the water. Pyrrole (0.21 mL, 0.003 mol) and poly(ethyleneoxide) lauryl ether (0.9 mL) were added to the solution and the solution was charged into the high-pressure reactor. The reactor was heated to 35 °C in a water bath, and carbon dioxide was then introduced into the reactor by an HPLC pump (JASCO SCF-Get). After stirring (1100 rpm) at 35 °C for 30 min at 12 MPa, the electrochemical polymerization was started by applying a constant voltage between the electrodes (Hokuto Denko, HSV-100). After the polymerization, CO₂ was slowly vented (0.4 MPa/min) using a back-pressure regulator (JASCO SCF-Bpg).

The electrochemical polymerization in water was carried out in the same reactor without adding CO₂. The amount of the solution was increased from 30 to 45 mL in order to immerse the electrodes during the polymerization. The solution of *p*-toluenesulfonic acid (0.5 mol/L) in water was prepared and sonicated for 15 min, then bubbled with nitrogen in order to exclude any oxygen dissolved in the water. To the high-

pressure reactor were added pyrrole (0.21 mL, 0.003 mol), poly(ethyleneoxide) lauryl ether (1.35 mL) and the solution of *p*-toluenesulfonic acid (45 mL). After stirring (1100 rpm) at 35 °C for 30 min without adding CO₂, the electrochemical polymerization was carried by applying a constant voltage (1.4 V) between the electrodes until the accumulated amount of charge reached 5 C.

2.6. Measurements

The thickness of the film was determined by a Surfcom 1400A surface texture measuring instrument (Tokyo Seimitsu, Tokyo, Japan). The polypyrrole film prepared on Pt electrodes was partially removed and the difference in the height between the polypyrrole film and the bare electrode surface was measured to determine the thickness of the film. The resistance of the film on the other side was measured by a 4-point probe method using a Loresta-GP with a MCP-TP06P probe (Mitsubishi Chemical Co., Tokyo, Japan). The resistance of the film was determined by the average of at least five data points. A constant resistivity correction factor (4.532) was used for the calculation of the conductivity (S/cm). The IR spectra were obtained using an FT-IR SPECTRUM 2000 spectrophotometer (Perkin-Elmer). The Raman spectra were measured using an FT/IR-800 equipped with an RFT-800 FT-Raman attachment (JASCO, Tokyo, Japan). An Nd/YAG laser (1064 nm, 4 W) was used for the measurements. The AFM images were obtained using a SPA300 scanning probe microscope (SII, Tokyo, Japan). The contact mode was used for the measurements. SEM pictures were obtained using a JSM-5900LV scanning electron microscope (JEOL, Tokyo, Japan). Confocal scanning microscopic images were obtained using a Laser Microscope 1LM21 (Lasertec, Yokohama, Japan). Surface roughness, Ra, was calculated by Salt 1.09 software (Mitani Corporation, Fukui, Japan). Ra calculated by the deviation of the data point from a standard surface level was averaged from five different positions. A small Ra suggests a flat and smooth surface. The accumulated amount of charge was controlled to ca. 5 C for each sample for the morphology study in order to minimize the difference caused by the thickness of the films. The outer surface of the film was examined for all microscopic measurements.

3. Results and discussion

3.1. Monitoring the emulsion and solubility of chemicals in supercritical carbon dioxide

Although carbon dioxide can be dissolved in water as a result of carbonate formation, supercritical carbon dioxide as a medium is essentially immiscible with water. The formation of the emulsion was visually monitored through sapphire windows in the high-pressure view cell. As shown in Fig. 2(a), large droplets were clearly observed in the high-pressure view cell in the mixture of supercritical carbon dioxide (12 MPa) and water in the absence of surfactants. The uniform emulsion formation was confirmed and the large

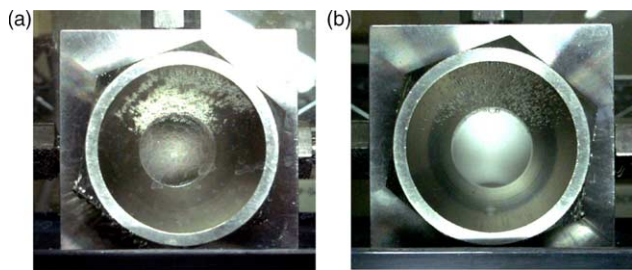


Fig. 2. Formation of supercritical carbon dioxide-in-water emulsion at 35 °C and 12 MPa. (a) Without surfactant; (b) with surfactant.

droplets were not observed during agitation (1100 rpm) when the surfactant was dissolved in water (Fig. 2(b)). It is clear that a supercritical carbon dioxide-in-water (C/W) emulsion is formed in the presence of the surfactant. The continuous water phase would enable an electrochemical reaction in the medium without adding polar organic co-solvents. The formed emulsion was not thermodynamically stable. A clear water phase was immediately observed in the lower part of the view cell after stopping the agitation and the boundary between the supercritical carbon dioxide and water gradually appeared within a few minutes. The thermodynamically unstable emulsion may give an additional process advantage for the electrochemical reactions. Dried films on the electrodes can be isolated without any drying processes if the electrodes are located in the upper phase of the carbon dioxide during the initial and final stages. It should be mentioned that the C/W emulsion was not formed in the absence of pressurized carbon dioxide. Dense carbon dioxide does play a crucial role as a second solvent for the formation of the emulsion.

The solubility of chemicals used in this study in supercritical carbon dioxide (35 °C, 12 MPa) was also qualitatively checked using the high-pressure view cell. Pyrrole was highly soluble in the supercritical carbon dioxide. The pyrrole droplets disappeared while adding liquid carbon dioxide. All supporting electrolytes examined in this study were essentially insoluble in supercritical carbon dioxide under that condition. Most of the droplets of the surfactant in water (25%) remained in the view cell during the solubility test at 12 MPa. However, the CO₂ phase became cloudy when the carbon dioxide was slowly released. Therefore, the solubility test of the neat surfactant extracted with chloroform was carried out in order to evaluate the solubility of the surfactant itself in supercritical carbon dioxide at 12 MPa. Although the surfactant was solid at 35 °C, the sample became liquid by the introduction of carbon dioxide. This phenomenon suggests that carbon dioxide penetrates into the surfactant and reduces the solute–solute interaction. The amount of the surfactant liquid decreased at 12 MPa, but more than half of the liquid remained in the view cell. It is clear that the surfactant has a limited solubility in supercritical carbon dioxide under this condition. On the other hand, the surfactant is highly soluble in water due to its high HLB (HLB = 14). Therefore, we assume that the surfactant mainly locates in the water phase and lowers the surface tension of the water and contributes to the formation of

the C/W emulsion under agitation at 1100 rpm, despite the limited solubility in the supercritical carbon dioxide.

3.2. Electrochemical polymerization

The electrochemical polymerization of pyrrole in the CO₂-in-water (C/W) emulsion was carried out in a high-pressure reactor with agitation at 1100 rpm, as shown in Fig. 1. Poly(oxyethylene) lauryl ether (C₁₂H₂₅(OCH₂CH₂)₁₅OH) (solution (25%) in water) was used as the surfactant to form the C/W emulsion. *p*-Toluenesulfonic acid (TsOH) was first used as the supporting electrolyte because the tosylate anion is known as one of the best dopants to produce the highly conductive polypyrrole [38]. Applying a constant voltage between the electrodes over 1.4 V started the electrochemical polymerization. A continuous current flow was observed during the polymerization, which implies that the resulting film is conductive. After a 100-s polymerization, a black polypyrrole film was formed on the anodic working electrode. It is reported that the potential of 0.6 V versus a saturated calomel electrode is the optimized potential for the electrochemical polymerization of pyrrole in water [38]. Since the polymerizations in this study were carried out by a two-electrode system without using reference electrodes, the applied voltage between the electrodes was controlled in order to optimize the electrochemical polymerization. Fig. 3 shows the effect of the applied voltage between the Pt electrodes on the electrochemical polymerization in the presence of *p*-toluenesulfonic acid. The apparent resistance between the electrodes decreased by increasing the applied voltage. Above 1.4 V, the conductivity of the film increased to more than 10 S/cm associated with the decreased resistance. This fact implies that the oxidation of pyrrole effectively proceeds to form the conducting polypyrrole above 1.4 V. The conductivity of the film prepared at the voltage of 1.4 V was

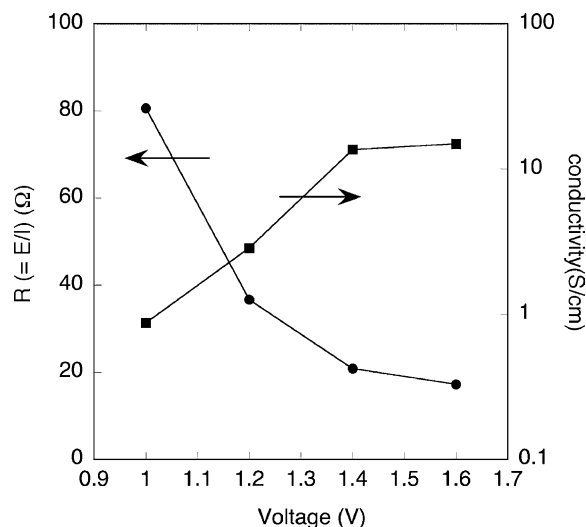


Fig. 3. Electrochemical polymerization of pyrrole in the C/W emulsion on Pt electrode. Pyrrole 0.1 mol/L; surfactant, C₁₂H₂₅(OCH₂CH₂)₁₅OH 3 vol%; supporting electrolyte, *p*-toluenesulfonic acid monohydrate 0.5 mol/L; CO₂, 12 MPa, 35 °C. The apparent resistance was calculated on the basis of the current at 5 s into the polymerization.

Table 1
Effect of supporting electrolytes on the electrochemical polymerization of pyrrole in supercritical carbon dioxide-in-water emulsion

Electrolyte	Concentration (M)	Voltage (V)	Conductivity (S/cm)	Dopant ^a (mol%)
Ts-OH ^b	0.1	1.5	4.61	26
Ts-ONa ^c	0.1	1.5	1.45×10^{-2}	18
DBS ^d	0.1	1.5	7.70×10^{-1}	23
LiBF ₄	0.1	1.5	6.79×10^{-6e}	NA
Ts-OH ^b	0.5	1.4	1.36×10	29

Electrochemical polymerization in the C/W emulsion was carried out at 35 °C and 12 MPa in the presence of poly(oxyethylene) lauryl ether (3 vol%). The accumulated amount of charge was controlled to 5 C. [Pyrrole]=0.1 M.

^a The amount of the dopant incorporated during the polymerization was calculated on the basis of the N/S ratio of the elemental analysis. Thick films prepared with 15 C were used for the elemental analysis.

^b Ts-OH, *p*-toluenesulfonic acid.

^c Ts-ONa, sodium *p*-toluenesulfonate.

^d DBS, sodium dodecylbenzenesulfonate.

^e The amount of charge was 9.8 C.

13.6 S/cm, which is comparable to the non-oriented polypyrrole films prepared in conventional solvents. The conductivity in this study is three times higher than that of the polypyrrole film prepared in supercritical carbon dioxide in the presence of acetonitrile as the cosolvent [31].

It is well known that the supporting electrolyte is simultaneously doped into the resulting film during the electrochemical polymerization, and therefore, strongly influences the electrochemical properties of the resulting polypyrrole [38–40]. Table 1 shows the effect of the supporting electrolytes on the conductivity of the resulting polypyrrole films prepared at the applied voltage of 1.5 V. The accumulated amount of charge was controlled to 5 C by changing the polymerization period. Among the examined electrolytes, *p*-toluenesulfonic acid (TsOH) produced a film with the highest conductivity from the electrochemical polymerization in the C/W emulsion. On the other hand, the conductivity of the film prepared with sodium *p*-toluenesulfonate (TsONa) was two orders of magnitude lower than that of the film prepared with TsOH. DBS and LiBF₄ also produced films with a low conductivity. It is reported that all of the electrolytes listed in Table 1 produce highly conductive polypyrrole films (10 – 10^2 S/cm) by electrochemical polymerization in water [38]. The current density after a 5-s polymerization was about 4.6, 1.0, 1.1 and 1.5 mA/cm² for the polymerization with TsOH, TsONa, DBS and LiBF₄, respectively. According to the current density, we assume that the dependence of the electrolyte on the conductivity of the resulting polypyrrole is caused by the difference in the continuous water phase in the C/W emulsion. The miscibility of the water in dense carbon dioxide may decrease with the addition of the ionic salt due to the increase in ionic strength of the water phase. Therefore, the resistance of the medium between the electrodes may become high, which makes the actual potential at the working electrode lower. When the concentration of TsOH was increased from 0.1 to 0.5 mol/L, the conductivity increased from 4.61 to 13.6 S/cm.

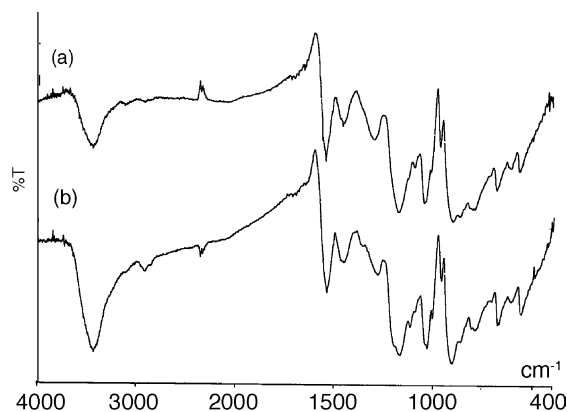


Fig. 4. IR spectra of the resulting polypyrrole films. (a) Prepared in the C/W emulsion; (b) in water.

The increase in conductivity is presumably due to the increased dopant concentration in the resulting polymer. Based on these results, electrochemical polymerization at the voltage at 1.4 V in the presence of TsOH at the concentration of 0.5 mol/L was used as the standard condition for the following discussions unless otherwise stated.

The structure of the resulting polypyrrole films was confirmed by IR and Raman spectroscopic measurements. The IR spectrum of the polypyrrole prepared in the C/W emulsion was consistent with that of the polypyrrole prepared in water, as shown in Fig. 4. The absorption bands attributed to the N–H stretching (3435 cm^{-1}), C–H stretching (2919 cm^{-1}), and skeletal vibration ($1541, 1457 \text{ cm}^{-1}$) modes are indicative of the pyrrole ring. The strong and broad absorption bands at 1168 and 1092 cm^{-1} are attributed to the S=O stretching mode of the *p*-toluenesulfonate. Fig. 5 shows the Raman spectra of the polypyrrole films prepared in the C/W emulsion or in water at 35 °C at an applied voltage of 1.4 V. The Raman spectrum of the polypyrrole film prepared in the C/W emulsion was also consistent with that of the polypyrrole prepared in water. The C=C stretching band at 1584 cm^{-1} implies the presence of the dication and radical cation [41,42]. The dication band was also observed at

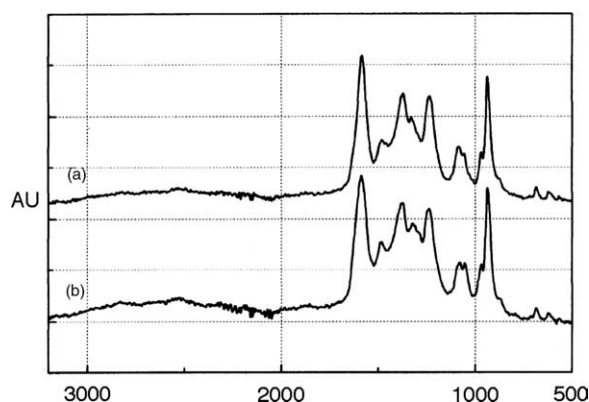


Fig. 5. Raman spectra of the resulting polypyrrole films. (a) Prepared in the C/W emulsion; (b) in water.

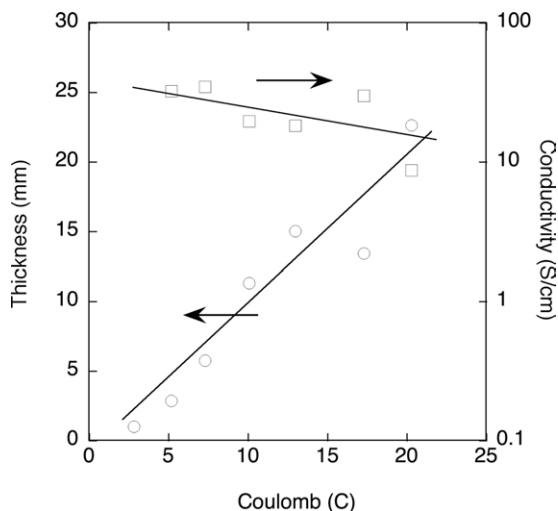


Fig. 6. Electrochemical polymerization of pyrrole in the C/W emulsion at 1.4 V. Pyrrole 0.1 mol/L; surfactant, $C_{12}H_{25}(OCH_2CH_2)_{15}OH$ 3 vol%; supporting electrolyte, *p*-toluenesulfonic acid monohydrate 0.5 mol/L; CO_2 , 12 MPa, 35 °C.

937 cm^{-1} which is attributed to ring deformation. The peak assigned to the radical cation was observed at 1088 cm^{-1} . According to the vibration spectra, the polypyrrole film prepared in the C/W emulsion has almost the same structure as the polypyrrole prepared in water. It is generally difficult to determine the structural defects of conducting polymers because most of the conducting polymers are insoluble in solvents. Presumably, the resulting polypyrroles are mainly composed of 2,5-substituted repeating units due to the similarity of the spectroscopic data. Supercritical carbon dioxide does not influence the structure and doping fashion of the resulting polypyrrole.

The thickness of the film could be controlled by the accumulated amount of charge during the electrochemical polymerization, as shown in Fig. 6. The conductivity of the films remained on the order of 10 S/cm in this thickness range.

3.3. Morphology of the polypyrrole films

The surface morphology of the polypyrrole film on platinum electrodes was investigated by microscopic measurements. In order to minimize the morphology change caused by the thickness of the films, the accumulated amount of charge was controlled to ca. 5 C during the electrochemical polymerization. Fig. 7(a) and (b) shows SEM images of the polypyrrole films prepared on platinum electrodes in the C/W emulsion and in water, respectively. A typical nodular structure was observed for both images. It seems that the grain size in Fig. 7(a) is homogeneous in comparison with Fig. 7(b). The AFM image of the same film prepared in the C/W emulsion is shown in Fig. 7(c). A distinctive cauliflower morphology was observed on the film. The individual nodule whose diameter was about $0.5\text{ }\mu\text{m}$ formed large nodules on a micron scale. Both microscopic experiments suggest that the polypyrrole prepared in the C/W emulsion has a homogeneous nodular structure.

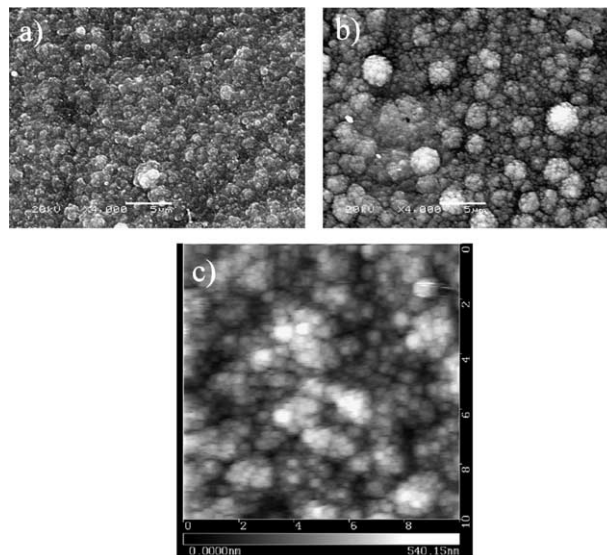


Fig. 7. Microscopic images of the polypyrrole film on platinum electrode prepared by the electrochemical polymerization at 35 °C. (a) SEM image of the film prepared in the C/W emulsion ($\times 4000$); (b) prepared in water ($\times 4000$); (c) AFM image of the film prepared in the C/W emulsion. Applied voltage: 1.4 V; $[TsOH]=0.5$, $[pyrrole]=0.1$ (mol/L), $[surfactant]=3$ (vol%).

A more noticeable difference was observed concerning the macroscopic morphology. Fig. 8 shows the surface and 3D images of the polypyrrole films measured by confocal scanning microscopy ($\times 400$). In Fig. 8(a), the nodules were spread out to form a fine uneven texture. On the other hand, irregular grains were observed on the film prepared in water (Fig. 8(b)). The surface roughness (R_a) of the polypyrrole prepared in the C/W emulsion was 2.20 mm which was higher than the R_a (1.76 mm) of the polypyrrole prepared in water. That is, the surface of the polypyrrole film prepared in the C/W emulsion is homogeneously rough.

The reason for the homogeneously rough surface is not clear and is under investigation. A nodular morphology is commonly observed on the polypyrrole films prepared on Pt electrodes [43–46]. A recent study by AFM microscopy showed that small nodules are formed even during the early stage of the electrochemical polymerization [46]. It is also reported that the surface morphology is influenced by the oxygen generated by the oxidation of water during the polymerization [45,47]. Since carbon dioxide is freely miscible with oxygen, the oxygen, which may be generated during the polymerization, can be efficiently removed from the electrode surface. Therefore, the formation of any unexpected nucleation or defects on the polypyrrole surface might be minimized by the presence of dense carbon dioxide in the reaction medium. Moreover, the carbon dioxide possibly affects the nucleation process itself. The carbon dioxide can penetrate into the polymer phase and reduce the interaction between the polymer chains. The penetration might significantly influence the nucleation process during the early stage of the polymerization. Although the reason for the homogeneously rough surface has not yet been determined, it seems that the nodules

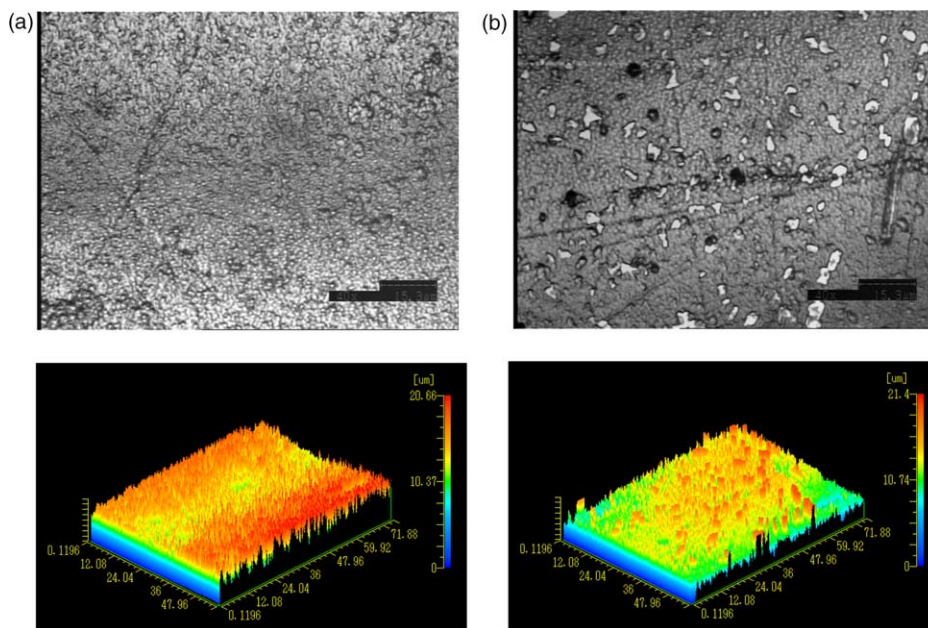


Fig. 8. Surface and 3D images of the polypyrrole films measured by a confocal scanning microscope: (a) prepared in the C/W emulsion; (b) prepared in water. Applied voltage: 1.4 V; [TsOH]=0.5, [pyrrole]=0.1 (mol/L), [surfactant]=3 (vol%).

formed during the early stage of the polymerization homogeneously grow during the polymerization in the C/W emulsion. We are now preparing very thin/thick polypyrrole films in the C/W emulsion, which may result in the formation of very flat or homogeneously rough films. Since polypyrrole is usually insoluble in all organic solvents, the morphology control during the preparation process is of prime interest from a practical viewpoint. The homogeneous rough morphology might be useful for certain applications, such as capacitors and sensors.

4. Conclusion

Although supercritical carbon dioxide itself is a non-polar solvent and immiscible with water, the addition of a surfactant to the water allows electrochemical polymerization in the supercritical carbon dioxide-in-water (C/W) emulsion. The electrochemical polymerization of pyrrole in the CO₂-in-water emulsion proceeded to form electron-conductive polypyrrole films. The conductivity of the resulting polypyrrole films was on the order of 10 S/cm, which is comparable to the polypyrrole films reported in the literature. Spectroscopic measurements indicated the formation of a polypyrrole doped with the *p*-tosylate anion. A fine uneven texture was observed on the polypyrrole film prepared in the C/W emulsion.

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