

原 著

## Synthesis of Polyaniline in Volcanic Hot Spring Water

Hiromasa Goto<sup>1)</sup>

(Received Apr. 6, 2010, Accepted Jul. 20, 2010)

### 天然火山性温泉水中でのポリアニリンの合成

後藤博正<sup>1)</sup>

#### 要 旨

導電性高分子であるポリアニリンを火山性天然温泉水中で合成し、その構造を赤外線吸収スペクトルで確認した。得られたポリアニリンの導電性は半導体領域であった。また電子顕微鏡観察で、このポリアニリンはナノファイバー状構造を形成していることが分かった。これより導電性ナノファイバーが温泉水中で得られることがわかった。本反応に用いた火山性天然水が、アニリンの重合反応およびナノファイバー形成に寄与する適切な pH 条件を提供したと思われる。本試みは高分子合成に天然資源を用いた新しい試みであると思われる。

キーワード：酸性、導電性高分子、ナノファイバー、酸性温泉水、ポリアニリン、走査型電子顕微鏡 (SEM)、電子スピン共鳴 (ESR)

#### Abstract

The conducting polymer polyaniline (PANI) was synthesized in natural volcanic hot spring water and its chemical structure was confirmed by infrared absorption spectroscopy. The PANI has electrical conductivity in the same range as that of semiconductors. The moderate acidity of volcanic hot spring water provides a favorable pH condition for polymerization of the aniline monomer. Scanning electron microscopy showed that the polymer has a nanofiber structure, demonstrating the synthesis of conductive nanofiber. This may be a new approach for the synthesis of organic electronics by employing natural resources.

Key words : Acidity, Conducting polymer, Nanofiber, Natural hot spring water, Polyaniline, Scanning electron microscopy (SEM), Electron spin resonance (ESR)

<sup>1)</sup> Graduate School of Pure and Applied Sciences, Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan. <sup>1)</sup> 筑波大学数理物質科学研究科物性・分子工学専攻 〒305-8573 つくば市天王台 1-1-1

## 1. Introduction

Since the discovery of conducting polymers, plastic electronics technology has been developed based on the synthesis and processing of conducting polymers. In particular, polyaniline (PANI), as one of the most promising organic conducting polymers (MacDiarmid and Epstein, 1994 ; Kuramoto and Tomita, 1997 ; Streltsov *et al.*, 2009 ; Nasybulin *et al.*, 2009 ; Immonen *et al.*, 2009 ; Wang J. *et al.*, 2010 ; Wang C.-C. *et al.*, 2009 ; Wei *et al.*, 2010), has been applied in industry as a buffer layer in electroluminescence (EL) devices, sensors (Janta and Josowicz, 2003) conductors (Ram *et al.*, 1994 ; Raghavendra *et al.*, 2003), solar cells (Tan *et al.*, 2004), for anti-corrosion (Lu *et al.*, 1995), and in composites (Mallick *et al.*, 2007 ; Aengin and Kalayci, 2010 ; Zngin *et al.*, 2002) and textiles (Wu *et al.*, 2009). PANI is generally prepared in a water medium with ammonium persulfate (APS) as an oxidizer. Aniline is treated with sulfuric acid for the formation of aniline sulfuric salt prior to addition of APS to initiate polymerization. Formation of the aniline salt is required for the synthesis of PANI.

Volcanic hot spring water (VW), as commonly found in hot springs, has been familiar to people in the world since ancient times. VW contains various minerals such as Mg, Ca, Zn, Al, Sr, Na, Li, Mg, Zn in the form of ions. Although the composition is dependent on the district, VW generally contain ions such as  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{HSO}_4^-$ , and the acidity of VW varies and is also location-dependent.

Aniline forms the aniline salt by reaction with sulfuric acid. The aniline salt can be converted into conducting polymer PANI by an oxidative polymerization mechanism. VW with low pH and sulfonate ions can be useful in the polymerization of aniline rather than employ sulfuric or hydrochloric acids. In this study, the synthesis of PANI in volcanic hot spring water was attempted, and the resulting chemical structure, generation of charge carriers, electrochemical properties, and optical properties were investigated. This method may provide a new objective for the application of natural resources in plastic electronics.

## 2. Experimental

### 2.1 Materials

Aniline monomer (Wako Chemicals, Japan) was purified by distillation prior to use. VW from Owakudani hot spring in Kanagawa (Japan) was employed in this research. The sample water was obtained on Feb. 16, 2009. APS (Kanto Chemical, Japan) was used as received. An analysis report of the VW is published via internet (Tsujiuchi, 1999). Analysis data, applicant for the analysis : Tsujiuchi, Owakudani hot spring water, 64.7°C, pH=2.9, electrical conductivity ( $\sigma$ )=2,770  $\mu\text{S}/\text{cm}$ , total amount of constituents=1,013 mg/kg, main cation ( $\text{Ca}^{2+}$ , 104 mg/kg ;  $\text{Na}^+$ , 43.1 mg/kg ;  $\text{Mg}^{2+}$ , 39.0 mg/kg), main anion ( $\text{SO}_4^{2-}$ , 447 mg/kg ;  $\text{Cl}^-$ , 124 mg/kg ;  $\text{HSO}_4^-$ , 18.6 mg/kg), type of hot spring source : acid-calcium · magnesium-sulfuric salt-chloride fountain, analysis date : July 29, 1999. Multi-channel type induced plasma coupling (ICP) analysis was carried out at the analysis center of University of Tsukuba (May 27, 2010). The analysis revealed that the water contains Li, Be, B, Na, Mg, Al, Si, S, Ca, Mn, Fe, Zn, Sr, and Ba.

## 2.2 Technique

Ultraviolet-visible (UV/Vis ; Hitachi U-2000) absorption spectra of the polymers in *N*-methylpyrrolidone (NMP) were measured. Infrared (IR) absorption spectra (Jasco FT-IR/300) of the polymers were obtained using the KBr method. Electron spin resonance (ESR) measurements of solid polymer samples were conducted using a JEOL JES TE-200 spectrometer with 100 kHz modulations (X-band). The spin concentration was determined using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as a standard. ICP analysis was carried out with PerkinElmer, Optima 7300DV. Scanning electron microscopy (SEM) observations were performed with a JEOL ED-SEM. The electrical conductivity of the polymers was measured at room temperature using the DC four-point probe method (Mitsubishi Lowrester-GP MCTP-T610 with MCP-TP06P probe).

## 2.3 Polymerization

We performed a series of six polymerizations in the VW with concentration variation of aniline (monomer) for obtaining PANI-1, PANI-2, PANI-3, PANI-4, PANI-5, and PANI-6 to examine reactivity of aniline in the VW and dependence of physical properties (electrical conductivity and spin concentration) of resultant polyaniline on the concentration in the polymerization reaction (Table 1).

Aniline (0.5 g) was added to the VW (20–250 mL) with stirring at room temperature. After 30 min, visual inspection confirmed that the aniline was completely dissolved in the water. The mixture was then continuously cooled to 0°C and APS (1.845 g, 8 mmol) was gradually added to the solution (Fig. 1). Here, polymerization of aniline is usually performed at 0–5°C because higher temperature causes cross link reaction for the resultant polyaniline. The cross-linking results in two dimensionally propagated materials, which shows black color and very low electrical conductivity. Conducting polymers require one-dimensional skeleton due to requirement of generation of polarons and bipolarons as charge carriers. Fraction of two-dimensional structure for the conducting polymer depresses conductivity in the entire sys-

Table 1 Polymerization<sup>a</sup> of aniline in volcanic hot spring water, and results of electrical conductivity and spin concentration.

Sample	Water <sup>b</sup> (g)	Monomer (g) <sup>c</sup>	Quantity (g) <sup>d</sup>	<i>T</i> (°C) <sup>e</sup>	$\sigma$ (S/cm) <sup>f</sup>	<i>N</i> <sub>s</sub> (spins/g) <sup>g</sup>
PANI-1	20	0.5	0.514	0	$5.4 \times 10^{-4}$	$1.4 \times 10^{20}$
PANI-2	50	0.5	0.503	0	$5.3 \times 10^{-4}$	$1.3 \times 10^{20}$
PANI-3	100	0.5	0.495	0	$5.8 \times 10^{-4}$	$1.1 \times 10^{20}$
PANI-4	150	0.5	0.456	0	$2.3 \times 10^{-4}$	$1.2 \times 10^{20}$
PANI-5	200	0.5	0.458	0	$2.4 \times 10^{-4}$	$1.1 \times 10^{20}$
PANI-6	250	0.5	0.469	0	$9.3 \times 10^{-5}$	$1.0 \times 10^{20}$
PANI-RT	200	0.5	0.468	25	$1.6 \times 10^{-4}$	$1.3 \times 10^{20}$
PANI-50°C	200	0.5	0.376	50	$4.5 \times 10^{-7}$	$7.3 \times 10^{19}$
PANI-Ca	200 <sup>h</sup>	0.5	0.540	0	$5.0 \times 10^{-3}$	$1.9 \times 10^{20}$

<sup>a</sup> Ammonium persulfate=1.845 g (8 mmol). <sup>b</sup> Volcanic hot spring water. <sup>c</sup> Aniline. <sup>d</sup> Quantity of resultant polyaniline. <sup>e</sup> Polymerization temperature. <sup>f</sup> Electrical conductivity. <sup>g</sup> Spin concentration. <sup>h</sup> Small amount of sulfuric acid was added to the reaction mixture to prepare the same pH value as the spring water sample (pH 2.9) employed in this study after addition of  $\text{CaCl}_2$  (0.4 g).

tem. While, in the present study, we attempted polymerization of aniline at room temperature and 50°C (hot spring water temperature) to examine dependence on reaction temperature in view point of natural temperature of VW (resultant polymer : PANI-RT and PANI-50°C, Table 1). Further, polymerization under a presence of  $\text{CaCl}_2$  was carried out to examine if  $\text{Ca}^{2+}$  ion as the main cation in the VW contributes the reaction.

All of the solutions color changed from dark brown to dark green in the polymerization over time. After 24 h, the dark green solution with metallic reflection was filtered. The filtrate was thoroughly washed with excess distilled water and excess methanol at room temperature. The dark green material thus obtained was dried under vacuum to yield PANI. The constituents and their quantities used for the polymerizations are summarized in Table 1. The pristine PANIs are in the oxidized (doping) state (Fig. 1). Here, the counter anion can be mainly  $\text{SO}_4^{2-}$  and  $\text{HSO}_4^-$  because these are main anions in the VW. In the polyaniline chemistry, it is generally known that sulfuric acid is statically coupled with nitrogen atom of aniline.

Quantity of the resultant polyaniline are higher than that of monomer amount employed for the polymerization, i.e., PANI-1 (monomer=0.5 g, resultant polyaniline=0.514 g). This is because the resultants possess APS and counter anion as dopants in general. Therefore, estimation of exact synthetic yield after the polymerization is limited in the chemistry of polyaniline. However, reduction of the doped polyaniline (as prepared polymer) by using hydrazine allows dedoping. The synthetic yield might be obtained by this method.

Quantity of resultant polyaniline is slightly decreased with decreasing the concentration of the monomer in the VW in the polymerization (Table 1). This result suggests that decrease of the concentration depresses the reaction activity of the monomer. However, the small decrease is tolerable for practical applications.

The change in pH of the PANI-2 polymerization solution was monitored during the reaction as a function of time (Fig. 2). The pH increased after addition of the aniline monomer, because the aniline monomer is coupled with ions in the VW. The pH value then decreased after addition of APS. An inflection point is observed at around  $1 \times 10^4$  s. The pH value decreased with time, increases slightly at  $1.66 \times 10^4$  s (Fig. 2, inset), and then gradually decreases. The decrease of the pH value in the reaction corresponds to the progress of the polymerization. Although the polymerization rate is somewhat low compared to the polymerization reaction of aniline with acetic acid and sulfuric acid (Konyushenko *et al.*, 2009), the profile obtained in this research is characteristic of the polymerization behavior of aniline monomer

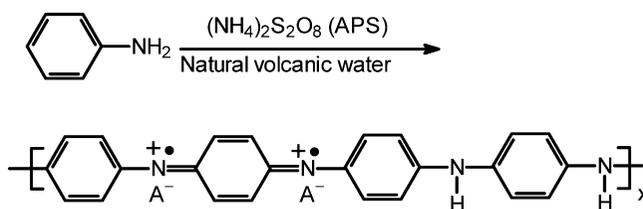


Fig. 1 Polymerization of aniline in volcanic hot spring water.

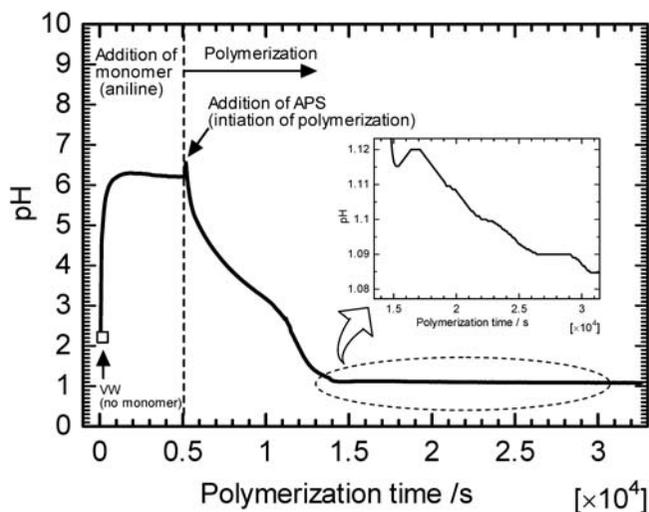


Fig. 2 Change in pH as a function of polymerization time. Inset shows enlarged profile.

and confirms that the polymerization of aniline progressed in VW. The polymerization rate can be improved by addition of large amount of oxidizer to the reaction mixture or metal ions such as  $\text{Ca}^{2+}$ .

### 3. Results and discussion

#### 3.1 UV/Vis optical absorption

Figure 3 displays the UV/Vis optical absorption spectrum of a PANI-2 solution in NMP. The absorption band at 626 nm is a doping band. The band at 324 nm is due to the  $\pi-\pi^*$  transition of the benzene ring in the polymer. Other polymers synthesized in the VW show the same absorption band. This result indicates that the PANIs were successfully prepared in the VW. It should be noted that this spectral form is the typical PANI emeraldine base (intermediate doping state). PANI-RT and PANI-50°C show the absorption peak at high energy region compared to the polymers prepared at 0°C. This can be due to the fact that the higher temperatures cause a cross-link reaction, and effective conjugation length of the resultant polyaniline is shortened. On the other hand, the reaction under the presence of calcium chloride allows the polymer (PANI-Ca) with absorption maximum at long wavelengths. Also, quantity of the resultant polyaniline under the presence of calcium chloride is the highest in the series of the polymerization (Table 1). This result implies that the calcium chloride aids progress of the present polymerization. In other words, the calcium chloride may play a role of auxiliary agent for the aniline polymerization.

#### 3.2 Infrared (IR) optical absorption

Infrared (IR) optical absorption of the PANIs was examined using the KBr method, and the results are shown in Fig. 3. The absorption band at  $1,570\text{ cm}^{-1}$  is ascribed to the quinoid

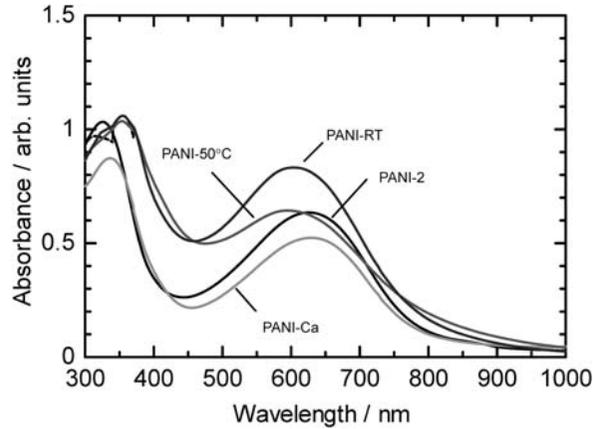


Fig. 3 UV/Vis optical absorption spectra of PANIs in *N*-methylpyrrolidone (NMP) solution.

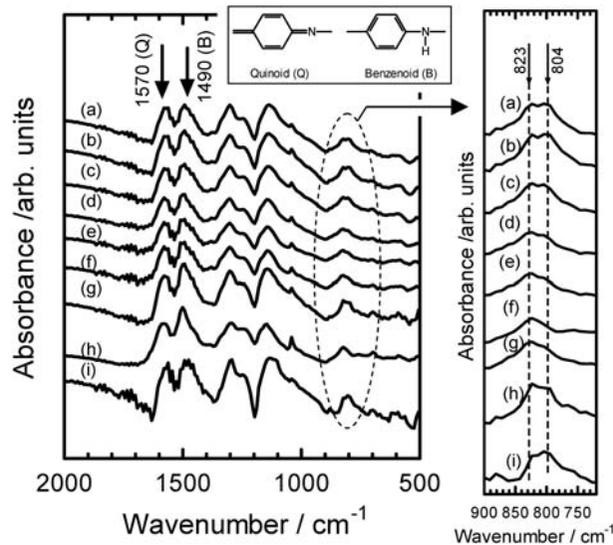


Fig. 4 IR spectra of PANIs in various concentrations of hot spring water. (a) PANI-1, (b) PANI-2, (c) PANI-3, (d) PANI-4, (e) PANI-5, (f) PANI-6, (g) PANI-RT. (h) PANI-50°C, and (i) PANI-CaCl<sub>2</sub>. Inset shows the quinoid and benzenoid structures in the PANI main chain. (Right) IR absorption signals at 804 and 823 cm<sup>-1</sup>.

structure (Q) in the main chain, and that at 1,490 cm<sup>-1</sup> is due to the benzenoid structure (B) (Fig. 4, inset). The quinoid structure in the polymer reflects increase of electrical conductivity accompanied by increase of charge carrier because generation of the charge carrier in the main chain produces quinoid structure. The intensity ratio (1,570 cm<sup>-1</sup>/1,490 cm<sup>-1</sup>) is almost constant for PANI-1, PANI-2, PANI-3, PANI-4, PANI-5, PANI-6. However, PANI-RT and PANI-50°C show low absorption intensities for the quinoid structure. The band at 1,301 cm<sup>-1</sup> is assignable to the CN stretching vibration of the quinoid-benzenoid-quinoid (QBQ) sequence. The

absorption band at  $1,241\text{ cm}^{-1}$  is due to C-N stretching in the benzene-benzene-benzene (BBB) sequence (tang *et al.*, 1988). Absorption bands at  $804$  and  $823\text{ cm}^{-1}$  are ascribed to C-H out-of-plane vibrations on the aromatic main chain. The intensity of the band at  $804\text{ cm}^{-1}$  decreased with the decrease in the concentration of monomer in the polymerization (Fig. 4 (right), (a)= $0.28\text{ M}$ , (f)= $0.02\text{ M}$ ). This result may be related to the length of the main chain or content of Q in the main chain. PANI-Ca shows relatively strong absorption band at  $804\text{ cm}^{-1}$ . Characteristic absorption band at  $1,140\text{ cm}^{-1}$  was assigned as an electronic-like band (delocalization of electrons on the PANI main chain) related to the electrical conductivity (Yamauch, 1992). Basically, all of the PANI samples had the same characteristic absorption IR bands of standard PANI (Quillard *et al.*, 1994).

### 3.3 Electron spin resonance (ESR)

The pristine PANI thus synthesized is partly in the oxidized (doping) state. It has charge carriers (polarons (cation radical) and bipolarons (dication)), and exhibits electrical conductivity. ESR measurements can evaluate the presence of charge carriers in PANI. A representative ESR spectrum for the PANI in this study is shown in Fig. 5. The spectrum is a symmetrical Lorentzian absorption with  $\Delta H_{1/2}/\Delta H_{pp}=2.77$ . The inset of Fig. 5 indicates  $\Delta H_{1/2}$  (line width at half maximum) and  $\Delta H_{pp}$  (peak-to-peak line width) in the ESR signal (Konyushenko *et al.*, 2006). The spin concentration ( $N_s$ ) is increased with the concentration of monomer in VW water during the synthesis of PANI. This result may correspond to the increase in the molecular weight of PANI with increasing monomer concentration during synthesis, because of an increase in reactivity. The  $g$ -values are almost constant, which indicates that the charge carriers are polarons and the species are not changed if the concentration of monomer is

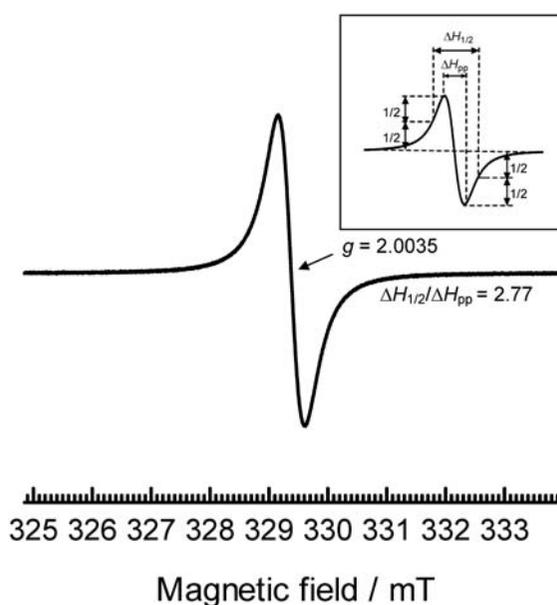


Fig. 5 ESR spectrum of PANI-1. Inset shows  $\Delta H_{1/2}$  and  $\Delta H_{pp}$  in the spectrum.

altered during the polymerization reaction, as shown in Fig. 6. Especially, PANI-Ca shows the highest spin concentration. This result is consistent with the IR (the strong absorption band at  $804\text{ cm}^{-1}$ ) and optical absorption measurements results (absorption peak located at the longest wavelengths in the samples).

### 3.4 Electrical conductivity

The electrical conductivity of compressed pellet samples of the as-prepared PANI was measured. The conductivity of compressed PANI pellets vs. concentration of monomer during PANI synthesis is shown in Fig. 7. The conductivity of the resultant PANI was increased with the concentration of monomer and the value is saturated at around  $5 \times 10^{-4}\text{ S/cm}$ . PANI-50°C shows low electrical conductivity may be due to occurrence of cross-link reaction in the polymerization. PANI-Ca displays good electrical conductivity ( $5.0 \times 10^{-3}\text{ S/cm}$ ). This is consistent with the results of the IR and the optical absorption.

### 3.5 Surface structure

A polarized differential interference contrast microscopy (DIM) image of PANI-2 (compressed pellet) is shown in Fig. 8 (a). The low magnification image suggests that the surface consists of fine particles. An SEM image of the PANI-2 is shown in Fig. 8 (b). The high magnification reveals that PANI-2 forms a fiber structure ; the fiber diameter is approximately  $150\text{ nm}$  and the longest fiber in the micrograph is longer than  $4.7\text{ }\mu\text{m}$ . Fiber formations can be due to aggregation during the PANI synthesis. PANI nanostructures have been prepared in the presence of weak organic acid (Tran *et al.*, 2008) or in polymeric acid solution (Zhang *et al.*, 2007). Fundamentally, the fiber shape of the polyaniline thus synthesized in the present study is the same as the previously reported method by using camphor sulfonic acid, or naphthalene sulfonic acid (instead of use of sulfuric acid). Here, the standard polymerization method generally produces non nano-fiber structure (non order structure). While, the polyaniline thus prepared in the VW displays long nano-fiber, as shown in Fig. 8 (b) (dashed line : trace of the longest fiber in the image). The nano-fiber is relatively longer in size than that of the polyaniline nano-fiber produced by the combination of APS and

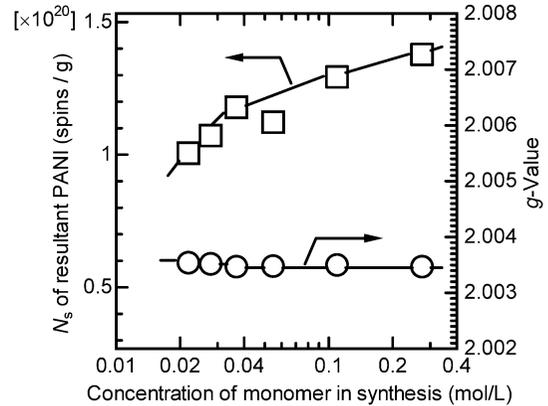


Fig. 6 ESR results for the PANIs. Spin concentration ( $N_s$ ) vs. aniline monomer concentration in the polymerization reaction ( $\square$ ) and g values ( $\circ$ ).

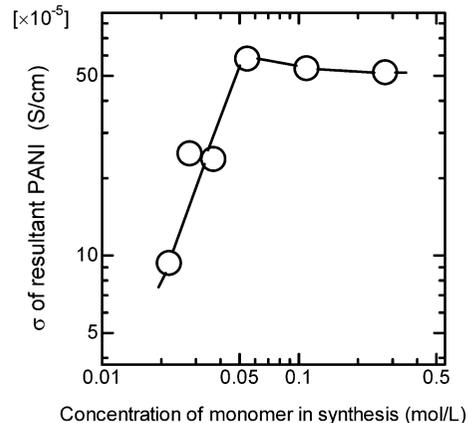


Fig. 7 Conductivity ( $\sigma$ ) of compressed PANI pellets as a function of the aniline monomer concentration in the polymerization reaction.

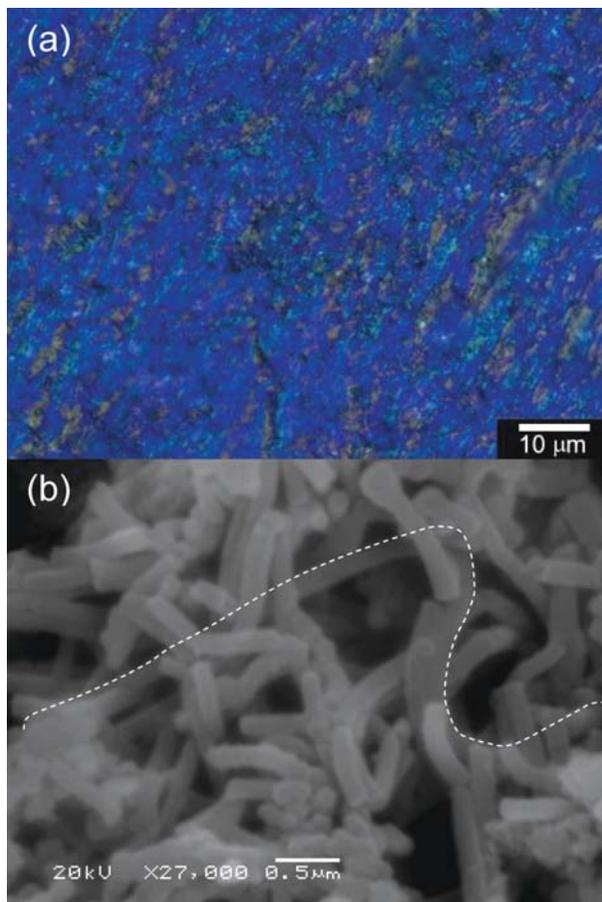


Fig. 8 (a) Polarizing differential interference contrast microscopic image (DIM) of a compressed pellet sample of PANI-2 ( $\times 500$ ). (b) SEM micrograph of the PANI-2 bulk sample ( $\times 27,000$ ). Dashed line : trace of the longest fiber in the image.

camphor sulfuric acid at appropriate condition. The results in this research demonstrate that the VW provides satisfactory condition for formation of PANI nano-fiber having moderate electrical conductivity, without use of any complicated preparation for the reaction medium (i.e., operation of adjustment of pH).

#### 4. Conclusion

PANI was synthesized in natural volcanic hot spring water. Infrared absorption spectra of the synthesized product confirmed the chemical structure of PANI. The moderate acidity of the water provides a good environment for the polymerization of aniline monomers. Furthermore, a set of the results suggests that change in amount of the VW as a reaction solvent for the polymerization allows tuning of spin concentration and electrical conductivity of the resultant polyaniline. The polymerization at 25°C afforded the polyaniline with the moderate

electrical conductivity. Quasi-model experiment implies that calcium in the natural volcanic hot spring water behaves auxiliary agent to promote the polymerization. Although we need to perform further research to evaluate a role of metal ions, employment of the natural volcanic hot spring water in this study gave us the new clue for development of conducting nanofiber with high performance in electro-magnetic properties.

Natural volcanic hot spring waters from other places may give another polymerization results because the constituent depends on location. This method may provide a new approach toward the synthesis of organic electronic materials by employing natural resources.

### Acknowledgments

The author thanks Hakone Hot Spring Spa Supply Co. Ltd. (Kanagawa, Japan) for generously providing the hot spring water sample. The author is grateful to the Engineering Workshop of University of Tsukuba for glasswork and the Analysis Center for the ICP measurements.

### References

- Aengin, H. and Kalayci, G. (2010) : Synthesis and characterization of polyaniline/activated carbon composites and preparation of conductive films. *Mater. Chem. Phys.*, **120**, 46–53.
- Immonen, K., Nättinen, K., Sarlin, J. and Hartikainen, J. (2009) : Conductive plastics with hybrid materials. *J. Appl. Polym. Sci.*, **114**, 1494–1502.
- Janta, J. and Josowicz, M. (2003) : Conducting polymers in electronic chemical sensors. *Nat. Mater.*, **2**, 19–24.
- Konyushenko, E.N., Stejskal, J., Šedenkova, I., Trchová, M., Sapurina, I., Cieslar, M. and Prokeš, J. (2006) : Polyaniline nanotubes : conditions of formation. *Polym. Int.*, **55**, 31–39.
- Konyushenko, E.N., Trchová, M., Stejskal, J. and Sapurina, I. (2009) : The role of acidity profile in the nanotubular growth of polyaniline. *Chem. Paper.*, **64**, 56–64.
- Kuramoto, K. and Tomita, A. (1997) : Aqueous polyaniline suspensions : Chemical oxidative polymerization of dodecylbenzene-sulfonic acid aniline salt. *Polymer*, **38**, 3055–3058.
- Lu, W.-K., Elsenbaumer, R.L. and Wessling, B. (1995) : Corrosion protection of mild steel by coatings containing polyaniline. *Synth. Met.*, **71**, 2163–2166.
- MacDiarmid, A.G. and Epstein, A.J. (1994) : The concept of secondary doping as applied to polyaniline. *Synth. Met.*, **65**, 103–116.
- Mallick, K., Witcomb, M. and Scurr, M. (2007) : Palladium-Polyaniline and Palladium-Polyaniline Derivative Composite Materials : A brief overview of their preparation and potential applications. *Plat. Met. Rev.*, **51**, 3–15.
- Nasybulin, E., Menshikova, I., Sergeev, V. and Levon, K. (2009) : Preparation of conductive polyaniline/nylon-6 composite films by polymerization of aniline in nylon-6 matrix. *J. Appl. Polym. Sci.*, **114**, 1643–1647.
- Quillard, S., Louarn, G., Lefrant, S. and MacDiarmid, A.G. (1994) : Vibrational analysis of polyaniline : A comparative study of leucoemeraldine, emeraldine, and pernigraniline bases, *Phys. Rev. B*, **50**, 12496–12508.

- Raghavendra, S.C., Khasim, S., Revanasiddappa, M., Prasad, M.V.N.A. and Kulkarni, A.B. (2003) : Synthesis, characterization and low frequency a.c. conduction of polyaniline/fly ash composites. *Bull. Mater. Sci.*, **26**, 733-739.
- Ram, M.K., Mehrotra, R., Pandey, S.S. and Malhotra, B.D. (1994) : AC conductivity of polyemeraldine base. *J. Phys. Cond. Matter.*, **6**, 8913-8922.
- Streltsov, A.V., Morozova, O.V., Arkharova, N.A., Klechkovskaya, V.V., Staroverova, I.N., Shumakovich, G.P. and Yaropolov, A.I. (2009) : Synthesis and characterization of conducting polyaniline prepared by laccase-catalyzed method in sodium dodecylbenzenesulfonate micellar solutions. *J. Appl. Polym. Sci.*, **114**, 928-934.
- Tan, S., Zhai, J., Xue, B., Wan, M., Meng, Q., Li, Y., Jiang, L. and Zhu, D. (2004) : Property influence of polyanilines on photovoltaic behaviors of dye-sensitized solar cells. *Langmuir*, **20**, 2934-2937.
- Tang, J., Jing, X., Wang, B., Wang, F. (1988) Infrared spectra of soluble polyaniline, *Synth. Met.*, **24**, 231-238.
- Tran, H.D., Wang, Y., D'Arcy, J.M. and Kaner, R.B. (2008) : Toward an understanding of the formation of conducting polymer nanofibers. *ACS Nano*, **2**, 1841-1848.
- Tsujiuchi, W. (1999) : Analytical Data of Hot Spring (Onsen Bunsekisho) of Owakudani Hot Spring. [http : //www.hakoneonsen.com/bunnseki.html](http://www.hakoneonsen.com/bunnseki.html) (checked in June, 2010).
- Wang, C.-C., Yang, S.-J. and Lee, H.-T. (2009) : Effects of interactions among polyaniline, dodecylbenzylsulfonic acid and silica on the morphology and properties of their sol-gel hybrids. *J. Polym. Res.*, **16**, 99-108.
- Wang, J., Yang, W., Tong, P. and Lei, J. (2010) : A novel soluble PANI/TPU composite doped with inorganic and organic compound acid. *J. Appl. Polym. Sci.*, **115**, 1886-1893.
- Wei, X., Jiao, L., Sun, J., Liu, S. and Yuan, H. (2010) : Synthesis, electrochemical, and gas sensitivity performance of polyaniline/MoO<sub>3</sub> hybrid materials. *J. Solid. State Electrochem.*, **14**, 197-202.
- Wu, J., Zhou, D., Looney, M.G., Waters, P.J., Wallace, G.G. and Too, C.O. (2009) : A molecular template approach to integration of polyaniline into textiles. *Synth. Met.*, **159**, 1135-1140.
- Yamauch, J. (1992) : *In* Estimation of materials with ESR, Eds : Ohya, H. and Yamauchi, p. 263, IPC publishing, Tokyo (in Japanese).
- Zhang, L., Peng, H., Hsu, C.F., Kilmartin, P.A. and Travas-Sejdic, J. (2007) : Self-assembled polyaniline nanotubes grown from a polymeric acid solution. *Nanotechnology*, **18**, 115607/1-115607/6.
- Zngin, H., Zhou, W. S., Jin, J.Y., Czerw, R., Smith, D.W., Echegoyen, L., Carroll, D.L., Foulger, S.H. and Ballato, J. (2002) : Carbon nanotube doped polyaniline. *Adv. Mater.*, **14**, 1480-1483.