Analysis of the Roles of Nitrogen and Oxygen in the Synthesis of an Alcohol Polymer during Plasma-Induced Reactions

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This paper investigates the roles of nitrogen and oxygen in forming a 1-butanol polymer. The analyses show that nitrogen is the key species for forming a stable 1-butanol polymer, and the viscosity of the polymer is increased as the ratio of nitrogen in the polymer is increased. In contrast, oxygen does not contribute to forming the polymer but rather prevents formation of the polymer instead. This article also analyzes the origin of C=O bonding in the 1-butanol polymer. IR analysis demonstrates that oxygen in the atmosphere is fixed in the polymer as C=O bonds, instead oxidizing the O−H group in 1-butanol.

Introduction

Recently developed electrical technologies have brought some new approaches for analyzing chemical reactions and forming new materials.[1−4] Important progress for the analysis of chemical reaction was achieved by Levis et al., using an ultrafast semiconductor switch.[5−7] This ultrafast switch made it possible to generate an intense pulse laser and successive excitation of the target molecules step by step.[5−7] Another useful development was the application of a pulse electric potential for accelerating electrons and exciting target molecules with electrons.[8−10]

Photon emission to the target molecules from a laser is suitable for analyzing the chemical reaction[11] because a laser is able to supply a precise amount of quantized energy to a target molecule and to excite the specific electron state in the molecules.[5−7] In particular, the application of a laser pulse also imparted a precise amount of energy per photon to a molecule and successfully achieved the selective bond dissociation and rearrangement of the molecule.[5] In contrast, emitting electrons is not suitable for analyzing the chemical reaction accurately because the kinetic energy of electrons inherently has some distributions, such as Maxwell−Boltzmann or Druyvesteyn distributions.[10] Nonetheless, the emission of electrons in an electric field has a great benefit when forming a new material instantaneously,[12,13] because excited electrons cause an electron avalanche and dissociate huge numbers of molecules through a chain reaction.[10,14]

Taking advantage of the merits of electron emission, we formed several alcohol-based polymers as the result of interactions between the emitted electrons and alcohol molecules in an asymmetrical pulse electric potential. Recent research revealed that hydrogen in alcohol was dissociated and produced hydrogen gas during the reaction.[15] Nitrogen in air was also dissociated and fixed in the alcohol polymer.[16]

However, these reactions were achieved in air, and the roles of nitrogen and oxygen for forming the alcohol polymer have
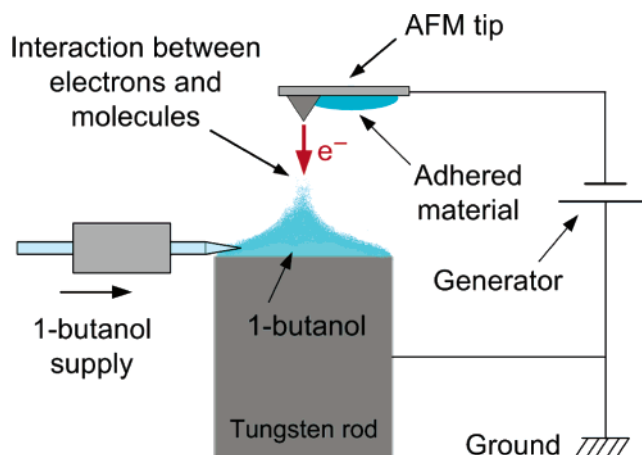

Figure 1. Open system for exciting and polymerizing 1-butanol molecules using electron emission in air. AFM tip, DF-20 (Au-coated silicon tip) SII. The experiments were performed in air at 26 °C temperature and 50% humidity. 1-Butanol, Wako Pure Chemicals, 99.5%.

not yet been determined. The origin of the characteristic IR peak of the C=O bond in the polymer is also unclear.

In this paper, we used a closed system to identify the roles of nitrogen and oxygen for the synthesis of a 1-butanol polymer. In the closed system, 1-butanol polymerizations were performed in different concentrations of nitrogen−oxygen gases for specifying their roles. The experiments in the closed system also helped determine whether oxygen in the air or in OH groups formed C=O bonding in the polymer. Before demonstrating these analyses, we summarize our current research.

Apparatus for Alcohol Polymerization in an Open System

Our current works for forming a 1-butanol polymer were achieved in an open system or in air.[17] Figure 1 illustrates an apparatus for synthesizing the 1-butanol polymer using electron emissions in an asymmetrical electric field.

The main components of the apparatus in Figure 1 were a pair of electrodes consisting of an atomic force microscope tip (AFM tip) and a tungsten rod covered with 1-butanol. These

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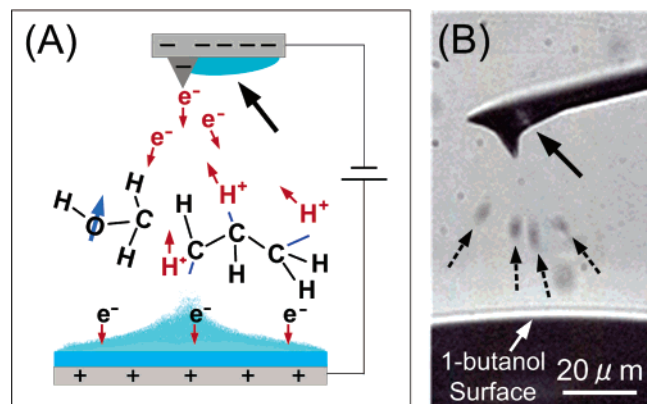‡ IR/Raman Group, Spectroscopy Department, Thermo Electron.

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Figure 2. Interaction between 1-butanol molecule and electrons emitted from an AFM tip in the open system (in air). (A) Model of the electrical interaction between 1-butanol molecule and electrons. (B) Optical image of the electrical interaction between electrons emitted from the AFM tip and 1-butanol molecules attracted to the tip. Their interaction was directly observed by the optical microscope in the form of microscale droplets as shown by the dotted black arrows. Four microscale droplets were observed in Figure 2B (dotted black arrows). AFM tip, DF-20 (Au-coated silicon tip) SII. 1-Butanol, Wako Pure Chemicals, 99.5%. Temperature, 26 °C. Humidity, 50%.

Figure 3. SEM image of the nitrogen-fixed 1-butanol polymer formed in the open system (in air). (A) Side view of the AFM tip covered with a 1-butanol polymer. (B) Front view of the polymer in Figure 3A. Black arrows in these figures indicate the swells of the 1-butanol polymer were expanded by the electron beam on the polymer. AFM tip, DF-20 (Au-coated silicon tip) SII. SEM, HITACHI S3500N.

electrodes were mounted on the *XYZ* stages for adjusting the relative position between the electrodes. A generator was connected between the electrodes, and a pulsed electric potential of 1.2 kV with a pulse width of 0.7 μs was applied at 15 kHz, using the AFM tip as a negative electrode. A 1 μL aliquot of 1-butanol was supplied to the tungsten electrode with a sharpened glass tube during the experiments. An optical microscope was equipped for directly observing 1-butanol polymerization reactions. The AFM tip, tungsten rod, and generator were connected to ground before each experiment to remove any electrical charge that could be released. The experiments were performed in air, and the temperature and humidity were 26 °C and 50%.

Reaction Mechanisms

The reaction mechanisms of 1-butanol polymerization are illustrated in Figure 2A,B. The core of the reaction was attributed to the dielectricity and volatility of 1-butanol molecule.

When an electric potential was applied between the AFM tip and the tungsten electrode (Figure 1), an electric field was generated between the electrodes.[18] Since the electrodes differed in size, an asymmetrical electric field was generated between them.[19] When dielectric molecules were placed between the asymmetrical electric field, the molecules were attracted to the more intense electric field toward the AFM tip.[19] Since the 1-butanol molecule had both dielectricity and volatility, it was ideal for inducing a molecular flow from the surface of 1-butanol on the tungsten electrode toward the very end of the AFM tip[17] (Figure 2A,B).

Once a molecular flow of 1-butanol was generated toward the very end of the AFM tip, it was possible to induce an interaction between the molecules and the electrons emitted from the tip. Since the electric capacity of the AFM tip was small, electrons on the tip could easily be emitted from the very top of the AFM tip if an electric potential of sufficient intensity was applied between the electrodes.[17,19]

In addition, if emitted electrons had enough kinetic energy, the electrons could interact with and decompose the 1-butanol molecules approaching the very end of the AFM tip. Figure 2A illustrates a model of this interaction and subsequent
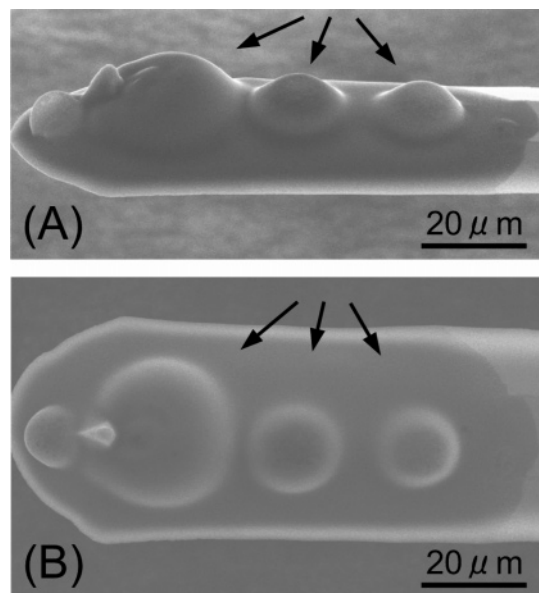
dissociation of a 1-butanol molecule.[5−7] The dotted black arrows in Figure 2B represent the optical image of the interaction between the 1-butanol flow from the surface of 1-butanol and the electrons emitted from the AFM tip. In our experiments, the alternative formations of nanoscale mist and microscale droplets (Figure 2B) were observed as a result of their interaction.[15−17]

The dissociated positive species, such as hydrogen ions and partially dissociated 1-butanol molecules, were electrically attracted to the negative AFM tip and deposited on the tip[15−17] (black arrows in Figure 2A,B). The deposited material was stable both in air and in a vacuum.[15−17]

The most important factor for alcohol polymerization was the generation of an appropriate electrical interaction between the emitted electrons and the alcohol molecules.[10,14] The interaction should also be achieved in a narrow area to synthesize the polymer efficiently. For these purposes, generating an asymmetrical electric field was the easiest approach. An ideal asymmetrical electric field satisfying these conditions was generated between an AFM tip and a tungsten rod, as illustrated in Figure 2B. The liquid alcohol covering the tungsten electrode also played important roles: the alcohol prevented both an uncontrollable violent discharge and combustion during the electron emission between the electrodes, as shown in Figure 2B.

Analysis of the Alcohol Polymer

Parts A and B of Figure 3 present scanning electron microscope (SEM) images of the material formed on the AFM tip. Figure 3A is a side view of the tip at an angle of 30°, and Figure 3B is a front view of the tip. The condition of the material was examined by emitting an electron beam onto the material with SEM in a vacuum. As shown by the black arrows in Figure 3A,B, the emitted areas selectively swelled. The formation of these swells demonstrated that the surface of the material was in a solid state. Palpation with a sharpened glass tube revealed that the inside of the material was also in a solid state when polymerization was achieved at a 1.2 kV electric potential.
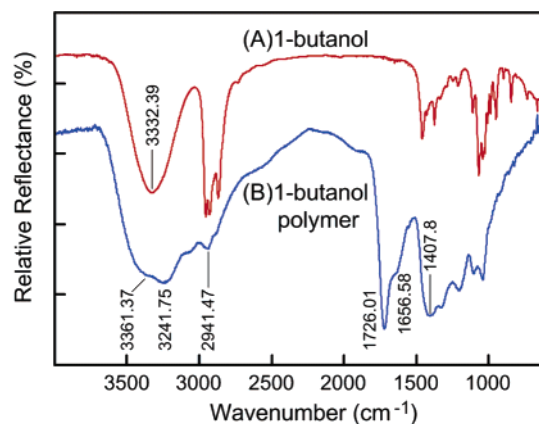
Figure 4. IR spectra of 1-butanol (A) and 1-butanol polymer (B). Microscopic FT-IR, Spectra-Tech, Inc., IRμs (II).

FTIR and EPMA analyses revealed characteristic structures of the material formed on the AFM tip. Parts A and B of Figure 4 present the IR spectra of 1-butanol and that of the material formed on the tip. A comparison of these spectra (Figure 4) indicated that 1-butanol molecules were dissociated during interaction with the emitted electrons (Figure 2A,B). In addition, the transition of an IR spectrum from relatively sharp peaks (Figure 4A) to round peaks (Figure 4B) indicated that the formed material on the AFM tip was polymerized and formed 3-D bridge structures.[10,14] In particular, FTIR analysis simultaneously detected 3241 (NH stretching), 1656 (NH_2 bending), and 1407 (CN bending) (1/cm). These peaks were characteristic spectra of nitrogen bonding and strongly suggested that nitrogen in air was fixed in the material on the AFM tip.

EPMA analysis detected 13−47% nitrogen in the material on the AFM tip, although analysis at this scale inherently involves experimental errors.[16] The result clearly demonstrated that nitrogen molecules in air were dissociated and fixed in 1-butanol as a new material. Since the viscosity of the material formed on the tip increased as the concentration of the fixed nitrogen increased, we hypothesized that the fixation of nitrogen in alcohol would enhance the stability of the material by forming stable 3-D bridge structures. We called the material a 1-butanol polymer.

EPMA analysis also detected 80 to 42% carbon and 6.4 to 10.1% oxygen from the 1-butanol polymer on the AFM tip.[16] In addition, micro-FTIR analysis detected an intense 1726 (1/cm) peak corresponding to the C=O bonding (Figure 4B). Carbon should originate from 1-butanol molecules. However, the sources of C=O bonding were not clear from these experiments performed in air. Some C=O bonds might have originated from OH groups in 1-butanol, and others might have come from the air.[10,14] As long as experiments were conducted in air, specifying the sources of C=O bonding would be difficult.

These analyses clearly demonstrated that conducting the experiments in a closed system was necessary to identify the roles of nitrogen and oxygen for 1-butanol polymerization and to specify the source of the C=O bonds in the polymer. In the following sections, we used a closed system to investigate the roles of nitrogen and oxygen for the synthesis of 1-butanol polymers and the source of C=O bonding in the polymer.

Apparatus for Alcohol Polymerization in a Closed System

A closed system depicted in Figure 5 was fabricated for maintaining the concentrations of nitrogen and oxygen in the system during 1-butanol polymerizations. It was necessary to
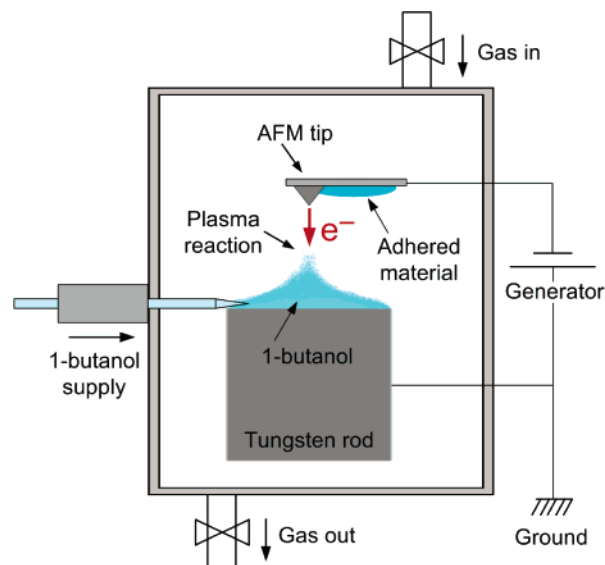

Figure 5. Closed system for forming the 1-butanol polymers using the electron emission in various gas conditions.

prepare three different concentrations of nitrogen−oxygen gases and compare the polymerizations in these gases in order to identify the roles of nitrogen and oxygen for forming the 1-butnaol polymers and to specify the source of C=O bonding in the polymer.

The main components of the closed system depicted in Figure 5 were identical to those of the open system presented in Figure 1. The apparatus in Figure 5 was shielded by a borosilicate glass so that the 1-butanol polymerization could be directly observed using an optical microscope. An electrical generator and a 1-butanol injector were employed outside the glass shield, as shown in Figure 5. An entrance and an exit of the nitrogen−oxygen mixed gas were installed on the glass shield so that the atmosphere in the closed system could be replaced with the adjusted gas. Stopcocks were provided at the entrance and exit for shielding the system after the adjusted gas was introduced.

The adjusted gases were prepared from high-purity gases of nitrogen and oxygen (N_2 > 99.9995%, O_2 < 0.5 ppm, CO < 1 ppm, CO_2 < 1 ppm, Tomoeshokai Co.; O_2 > 99.999%, N_2 < 2 ppm, CO < 0.5 ppm, CO_2 < 0.5 ppm, Tomoeshokai Co.). A standard gas consisting of 78.53% nitrogen and 21.47% oxygen (CO < 1 ppm, CO_2 < 1 ppm) was also used to set up a standard polymerization reaction.

Analysis of the Roles of Nitrogen and Oxygen

Influence of Nitrogen and Oxygen on the Electrical Interaction. The electrical interaction between the AFM tip and the surface of 1-butanol (Figure 5) was directly observed in the high-purity oxygen (O_2, 98.65%; N_2, 1.35%) and nitrogen (N_2, 99.78%; O_2, 0.22%). The purpose of this observation was to analyze the influences of nitrogen and oxygen on the electrical interactions and successive electron emissions between the tip and the surface of 1-butanol.

These observations were carried out in the closed system depicted in Figure 5, using the following procedures. The high-purity gas was introduced from the entrance of the shield at 500 mL/min and released from the exit into the air for 10 min, to replace the gas in the system with the high-purity gas. The stopcocks of the entrance and exit were closed at the same time to set up a closed system. A 1 μL aliquot of 1-butanol was introduced from the injector through a glass tube with an inner diameter of 5 μm. A pulse electric potential of 1.2 kV to 15

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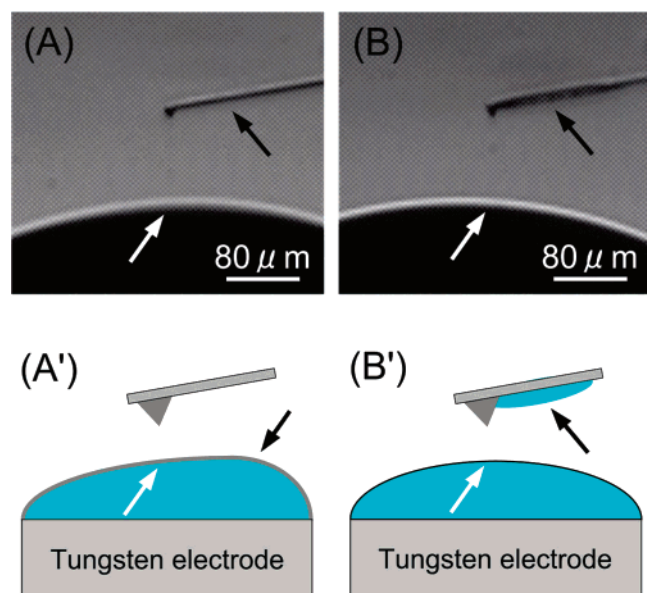*J. Phys. Chem. B, Vol. 109, No. 31, 2005* **14879**

Figure 6. Optical image of the electrical interaction between an AFM tip and the surface of 1-butanol in high-purity oxygen (A) and in high-purity nitrogen (B). The black arrows in A and B represent the negative AFM tips, and the white arrows represent the 1-butanol surface placed on the positive tungsten electrode. Parts A′ and B′ illustrate the corresponding images of A and B. The black arrow in A′ indicates the deformation of the 1-butanol surface as a result of the electrical interaction between the AFM tip and the surface of 1-butanol (white arrow). The black arrow in B′ represents the adhering 1-butanol polymer, which is observed only on the AFM tip placed in the high-purity nitrogen. The stable adhering material was not observed on the surface of the AFM tip placed in the high-purity oxygen. AFM tip, DF-20 (Au-coated silicon tip) SII. 1-butanol, Wako Pure Chemicals, 99.5%.

kHz was applied with a generator between an AFM tip and a tungsten rod covered with 1-butanol. The distance between the AFM tip and the 1-butanol surface was adjusted to 95 μm. The electric potential was applied for less than 1 min so that the concentration of high-purity gas in the closed system could be maintained at the initial state.

Parts A and B of Figure 6A,B represent optical images of the electrical interaction between the AFM tip (black arrows) and the surface of 1-butanol (white arrows) in high-purity oxygen (O$_2$ 98.65%, N$_2$ 1.35%) and nitrogen (N$_2$ 99.78%, O$_2$ 0.22%). Figures 6A′ and 6B′ correspond to Figures 6A and 6B.

When a pulsed electric potential of 1.2kV and 0.7μs was applied at 15 kHz between the AFM tip and the tungsten rod in high-purity oxygen (Figure 6A), the 1-butanol surface was slightly deformed due to the electrical interaction between the tip and the surface of 1-butanol. The surface of 1-butanol also started to blur when the electric potential was applied, as indicated by the white arrow in Figure 6A (see also Supporting Information). In contrast, the 1-butanol surface was not as deformed by the application of an identical electric potential in the high-purity nitrogen, and the surface of 1-butanol remained clear, as indicated by the white arrow in Figure 6B.

In addition, when the input electric current was 28 μA, the amount of the emitted electrons (electric current) detected at the tungsten rod in high-purity oxygen was 10.4 μA; however, in nitrogen it was 2.7 μA. These differences clearly demonstrated that the electrical interaction and resulting electron emission in high-purity oxygen (Figure 6A) were greater than those in high-purity nitrogen (Figure 6B).

These different electrical interactions and electron emissions could be attributed to the difference between the dissociation

energies of oxygen (5.13 eV) and nitrogen (9.78 eV). If identical electric potentials were applied to both of the high-purity gases, the same kinetic energy of electrons should originally be emitted from the AFM tip toward the surface of 1-butanol. However, the dissociation energy of nitrogen (9.78 eV) is much greater than that of oxygen (5.13 eV), and the emitted electrons in the nitrogen should lose more energy than those in the oxygen. Therefore, the emitted electrons in the oxygen (Figure 6A) should interact more violently with the surface of 1-butanol than those in the nitrogen (Figure 6B), as specified by the white arrows.

These different intensities of electron emissions could affect the composition of the 1-butanol polymers: The violent electron emission in the high-purity oxygen would prevent both 1-butanol molecules from approaching the AFM tip and the composition of 1-butanol polymer on the tip, due to the pressure of the electron emission. In fact, the material observed adhering to the AFM tip in high-purity nitrogen (Figure 6B, black arrow) was never observed in high-purity oxygen, as shown in Figure 6A.

As a result of these analyses, high-purity oxygen was replaced by 85.07% oxygen (14.93% nitrogen) in the following experiments so that the adhering material could be observed on the AFM tip, as shown in Figure 6B.

Analysis of the Roles of Oxygen and Nitrogen

1-Butanol polymerizations were performed in three different gases (oxygen-rich, standard, and nitrogen-rich) to identify the roles of nitrogen and oxygen for forming 1-butanol polymers. Oxygen-rich gas consisted of 85.07% oxygen and 14.93% nitrogen; standard gas consisted of 78.53% nitrogen and 21.47% oxygen; and nitrogen-rich gas consisted of 99.78% nitrogen and 0.22% oxygen. 1-Butanol polymerizations were performed in these gases according to the same procedures as applied to the high-purity atmosphere in the closed system in Figure 6. However, the distance between the AFM tip and the surface of 1-butanol was adjusted to 60 μm.

The 1-butanol polymerizations performed in the three different gases are depicted in Figures 2B and 6B. The materials adhering on the AFM tips were observed in these three experiments, as indicated by the black arrows in Figures 2B and 6B. However, the stabilities of these 1-butanol polymers varied greatly. The 1-butanol polymer adhering in the oxygen-rich condition was volatile: it immediately disappeared from the AFM tip (within 4 s), and never formed a stable compound. The 1-butanol polymer adhering in the standard gas was also initially volatile but gradually gained viscosity, becoming the most stable compound of the three after 35 s of electron emission. The 1-butanol polymer adhering in the nitrogen-rich condition was initially more stable than that in the standard gas, and it was easily deposited in the same amounts as in the standard gas in just 7 s. However, the polymer did not gain viscosity during the 35 s of application of the electric potential. The stability and viscosity were qualitatively examined by palpation with the use of a sharpened glass tube.[15]

Figure 7 presents the SEM images of the AFM tips after the polymerizations were performed in oxygen-rich and nitrogen-rich atmospheres. Parts A and B of Figure 7 present SEM images of the AFM tip used in the oxygen-rich atmosphere (85.07% oxygen and 14.93% nitrogen). Parts A′ and B′ of Figure 7 present the SEM images of the AFM tip used in the nitrogen-rich atmosphere (99.78% nitrogen and 0.22% oxygen). The 1-butanol polymer formed in the standard gas (data not shown) (78.53% nitrogen, 21.47% oxygen) looked similar to the one
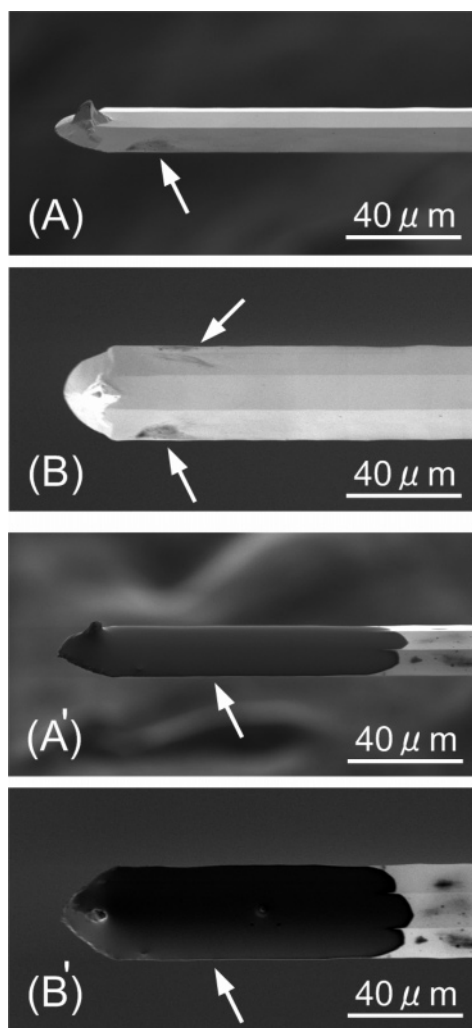
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Figure 7. SEM image of the AFM tips used for the 1-butanol polymerization. (A) Side view of the AFM tip used in the oxygen-rich atmosphere. (B) Front view of the AFM tip of A. (A′) Side view of the AFM tip used in the nitrogen-rich atmosphere. (B′) Front view of the AFM tip of A′. AFM tip, DF-20 (Au-coated silicon tip) SII.

TABLE 1: Weight Percent of Components in 1-Buthanol Polymers

	Gas Components	Emission time	Carbon	Nitrogen	Oxygen
1.	N₂: 14.9, O₂: 85.1	35 sec.	—	—	—
2.	N₂: 99.8, O₂: 0.2	7 sec. (35 sec.)	62.9	17.2	19.9
3.	N₂: 78.5, O₂: 21.5	35 sec.	55.6	24.9	18.5

formed in the nitrogen-rich atmosphere, as seen in Figure 7A′,B′ (99.78% nitrogen and 0.22% oxygen).

These SEM images clearly demonstrate that 1-butanol polymerization was not achieved in the oxygen-rich atmosphere (Figure 7A,B). However, 1-butanol polymer was obviously formed on the AFM tip when polymerization was performed in the nitrogen-rich and the standard atmospheres (Figure 7A′,B′, white arrows).

EPMA analyses were performed on the materials formed in the three different atmospheres to investigate the fixation of nitrogen. Table 1 presents the weight percent of components in the 1-butanol polymers on the AFM tips. Samples 1 and 2 in the table correspond to the polymers represented in Figure 7B,B′ (white arrows). Sample 1 (Figure 7A,B) was obtained in the oxygen-rich atmosphere during 35 s of electron emission. In this gas condition, no stable polymer was formed on the AFM

tip. Only a few remnants were observed on the tip (white arrows in Figure 7A,B), and EPMA could not detect the weight percent of the remnants.

Sample 2 (Figure 7A′,B′) was obtained in the nitrogen-rich atmosphere. The polymer was easily formed in just 7 s; however, the application of the electric potential was maintained for 35 s to adjust the experimental conditions. The sample on the AFM tip was stable both in air and vacuum (Figure 7A′,B′), and EPMA detected 62.9% carbon, 17.2% nitrogen, and 19.9% oxygen.

Sample 3 was obtained in the standard gas. The polymerization took 35 s for forming the same volume of a stable polymer as sample 2 (Figures 7A′,B′). Sample 3 on the AFM tip was more stable than sample 2, and EPMA detected 55.6% carbon, 24.9% nitrogen, and 18.5% oxygen.

From the relationships between the stability of 1-butanol polymer (Figure 6), the amounts of nitrogen fixed in the polymer (Table 1), and the length of electron emission for forming the stable polymer (Table 1), we concluded that nitrogen should be the key species for forming 3-D bridge structures and producing stable 1-butanol polymer. In contrast, oxygen did not contribute to forming the polymer. If anything, oxygen may prevent the forming of the polymer, or it may even decompose the produced polymer.

These conclusions were based on the facts that 1-butanol polymer was easily produced as the concentration of nitrogen in the atmosphere was increased from 14.9 to 99.8% and the stability of the polymer was enhanced as the concentration of nitrogen fixed in the polymer was increased from 17.2 to 24.9% (Table 1). In addition, the electron emission for forming the same amount of stable polymer became shorter (from 35 to 7 s) when the concentration of nitrogen in the atmosphere was increased from 78.5 to 99.8% (Table 1).

The same conclusions can also be supported from the viewpoint of oxygen concentration. 1-Butanol polymer was not formed as the concentration of oxygen in the atmosphere was increased from 21.5 to 85.1% (Table 1). Moreover, the electron emission for forming the same amount of stable polymer became longer (from 7 to 35 s) when the concentration of oxygen in the atmosphere was increased from 0.2 to 21.5% (Table 1).

These results confirmed that oxygen was an unfavorable species for the synthesis of the 1-butanol polymer. However, the experiments also demonstrated that the most stable 1-butanol polymer was formed in the standard gas with longer electron emission (35 s; Table 1) and that such a stable polymer could not be formed in the nitrogen-rich gas with shorter electron emission (7 s; Table 1).

The different lengths of electron emission came from the fact that the AFM tip in the nitrogen-rich atmosphere was covered with a stable 1-butanol polymer and interrupted the continuous electron emission in 7 s. In contrast, the AFM tip in the oxygen-rich atmosphere was not covered with the stable polymer as quickly, and the electron emission was sustained longer.

These observations and analyses indicated that oxygen should have removed unstable molecules, enhanced the concentration of nitrogen during the removal, and formed a stable 1-butanol polymer on the AFM tip. Therefore, oxygen should be an important species for sustaining electron emission and forming a stable polymer, although longer electron emission is required.

These different roles of nitrogen and oxygen may be attributed to their different electron orbits. Since carbon and nitrogen have more than three bonding orbits, they are suitable for forming stable 3-D bridge structures. In contrast, oxygen has only two bonding orbits; therefore, oxygen could interact with other atoms
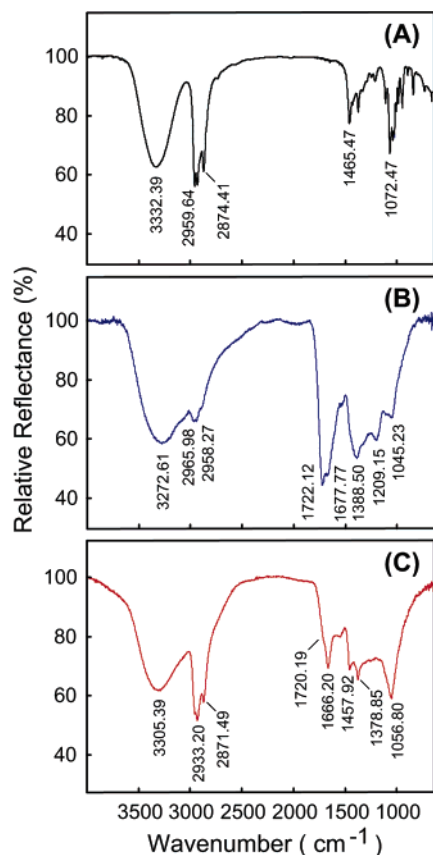
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Figure 8. IR spectra of 1-butanol and 1-butanol polymer. (A) IR spectrum of 1-butanol. (B) IR spectrum of 1-buthanool polymer formed in the standard gas (78.53% nitrogen and 21.47% oxygen). (C) IR spectrum of 1-butanol polymer formed in the nitrogen-rich gas (99.78% nitrogen and 0.22% oxygen). Microscopic FT-IR, Spectra-Tech, Inc., IRμs (II).

as a 2-D structure, or it could form a double bond such as C═O. Thus, oxygen could not produce stable 3-D bridge structures, but it could generally compose such gases as C═O, N═O, and O−C−O. The formation of these gases would also prevent the composition of 3-D alcohol polymers.

Moreover, oxygen in the closed system could be dissociated, becoming radicals or an ozone during the electron emissions.[10,14] The formation of these active species would also inhibit the instantaneous formation of a 1-butanol polymer and even dissociate the polymer. These assumptions are reasonable, since the dissociation energy and excitation energy of oxygen (5.13 eV) are much smaller that those of nitrogen (9.78 eV). As long as nitrogen was decomposed by the electron emission, the dissociation and excitation of oxygen was possible.

Analysis of the Origin of the C═O Bond in the Polymer

Micro-FTIR analysis was performed on the 1-butanol polymers formed in the standard gas and in the nitrogen-rich gas to identify the origin of C═O bonding in the polymer. The purpose of this analysis was to specify whether the oxygen in C═O bonding was fixed from the atmosphere or came from OH groups in 1-butanol molecules.

Figure 8A presents an IR spectrum of 1-butanol. Figure 8B illustrates an IR spectrum of 1-butanol polymer formed in the standard gas consisting of 78.53% nitrogen and 21.47% oxygen. The IR data corresponding to the EPMA data of sample 3 in Table 1 are represented by the blue line. Figure 8C is an IR spectrum of 1-butanol polymer formed in the nitrogen-rich gas consisting of 99.78% nitrogen and 0.22% oxygen. The IR data
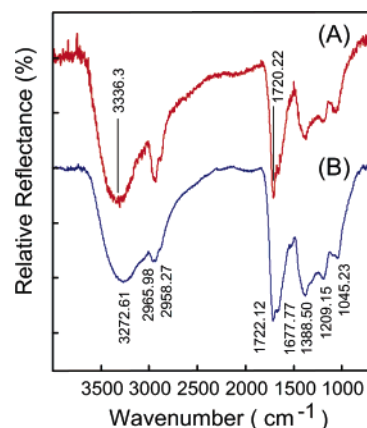

Figure 9. IR spectra of 1-butanool polymer formed in 7 s in the standard gas (A) and 1-butanol polymer formed in 35 s in the nitrogen-rich gas (B). Microscopic FT-IR, Spectra-Tech, Inc., IRμs (II).

corresponding to the EPMA data of sample 2 in Table 1 are represented by the red line.

An intense C═O peak was detected at 1722 (1/cm) from the 1-butanol polymer formed in the standard gas (78.53% nitrogen, 21.47% oxygen), as shown in Figure 8B. The formation of an intense C═O peak indicates that a huge number of C═O bonds were formed in the polymer during 1-butanol polymerization. In contrast, the C═O peak was not detected in the 1-butanol polymer formed in the nitrogen-rich gas (99.78% nitrogen, 0.22% oxygen), as shown in Figure 8C. Only a slight shoulder was recognizable at 1720 (1/cm). Therefore, the most straightforward interpretation of these spectra is that the C═O bonding fixed in the polymer was primarily from oxygen in the atmosphere.

In addition, the IR spectrum without an intense C═O peak (Figure 8C) clearly demonstrated that the origin of the C═O bonding should not be an OH group. If the OH group in 1-butanol was the main source of C═O bonding, an intense C═O peak should have appeared at 1720 (1/cm) in Figure 8C. However, such an intense C═O peak was not detected from the 1-butanol polymer. This analysis also supported that the C═O bonding originated from oxygen in the atmosphere.

However, we have to consider the different lengths of "net" electron emission for forming the 1-butanol polymers in Figure 8B,C. The polymer in Figure 8B was formed by 35 s of electron emission in the standard gas. In contrast, the polymer in Figure 8C was formed by 7 s of electron emission in the nitrogen-rich gas. These different lengths of electron emission could affect the formation or concentrations of C═O bonds in the polymers. Therefore, the IR spectra in Figure 8B,C should be compared by the polymers formed in the same length of electron emission for concluding that the origin of C═O bonding was definitely the oxygen in the atmosphere.

Parts A and B of Figure 9 present the IR spectra of the 1-butanol polymers formed in 7 s (Figure 9A) and in 35 s (Figure 9B) of electron emission in the standard gas (78.53% nitrogen, 21.47% oxygen), with other conditions being identical. Although the relative reflectance of these IR spectra did not represent the actual intensity, the IR spectrum obtained for 7 s of electron emission (Figure 9A) clearly demonstrated the formation of C═O bonding at 1720 (1/cm). A comparison of the IR spectra between Figure 9A obtained from the polymer in standard gas in 7 s and Figure 8C obtained from the polymer in nitrogen-rich gas in 7 s clearly indicates that the length of the electron emission was not the primary factor for the formation of a C═O bond. Therefore, we can conclude that the
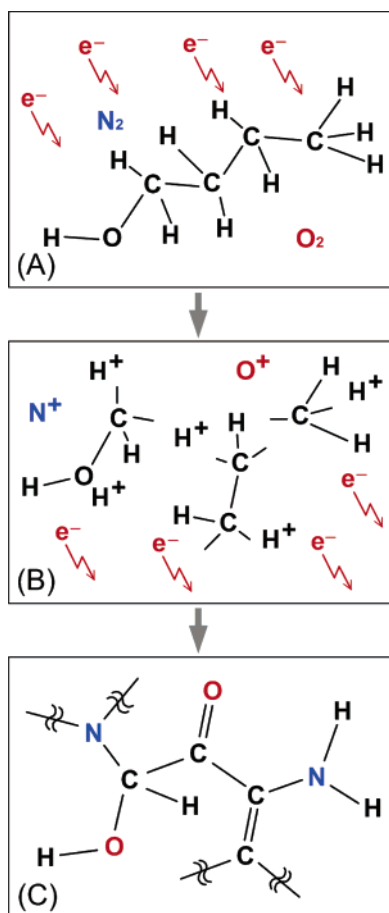
Figure 10. Image of possible 1-butnaol polymerization reaction. (A) Emitted electrons are approaching 1-butanol, nitrogen, and oxygen. (B) Electrons with enough kinetic energy dissociate 1-butanol, nitrogen, and oxygen and produce ions and radicals. (C) Possible structure of 1-butanol polymer as a result of electrical neutralization of positive species on the negative AFM tip.

origin of the C═O bond was oxygen in the atmosphere instead of the OH group in 1-butanol molecules.

The transition of IR spectrum (Figure 9A,B) also showed that the relative intensities of 3268 (NH stretching), 1664 (NH_2 bending), and 1392 (CN bending) (1/cm) with respect to OH peak (3336 cm^{-1}) (Figure 9A) were enhanced as the length of electron emission was increased. The intensity of a 1720 (1/cm) peak was also enhanced with respect to the OH peak (3336 cm^{-1}) as the length of electron emission was increased. These IR transitions also indicate that nitrogen and oxygen in the atmosphere were fixed in the 1-butanol polymers.

Based on the analyses so far, an image of 1-butanol polymerization is presented in Figure 10. The emitted electrons with sufficient kinetic energy dissociated not only 1-butanol but also oxygen and/or nitrogen in the atmosphere (Figure 10A,B). These electrical interactions mainly produced positive species through electron avalanches.[10,14] The positive species consisted of ions and radicals from hydrogen, nitrogen, oxygen, and partially dissociated 1-butanol (Figure 10B). These positive ions and radicals would be attracted to the negative AFM tip through Coulomb interaction and would be electrically neutralized on the tip.

If the amount of nitrogen exceeds that of oxygen in the atmosphere (99.78% nitrogen, 0.22% oxygen), a relatively stable 1-butanol polymer would be synthesized almost immediately (in 7 s). The stable polymer should consist of 3-D bridge structures and primarily consist of carbon and nitrogen fixed in

the polymer (Figure 10C). However, if the amount of oxygen exceeds that of nitrogen (85.07% oxygen, 14.93% nitrogen), stable 3-D bridge structures could not be formed and unstable oxygen-based molecules would evaporate in the atmosphere. On the other hand, if the ratio of nitrogen to oxygen was 78.53% to 21.47%, the role of nitrogen to form stable 3-D bridge structures and the role of oxygen to remove the unstable species would synthesize the most stable 1-butanol polymer, although the polymerization would take longer.

Summary

We analyzed the roles of nitrogen and oxygen in forming the 1-butanol polymers. The origin of C═O bonding in these polymers was also investigated. These analyses were achieved in different concentrations of nitrogen−oxygen atmospheres with the use of a closed system.

Different intensities of the electrical interactions between the AFM tip and the surface of 1-butanol were observed in different concentrations of nitrogen−oxygen gases. The electrical interaction and resulting electron emission in oxygen-rich gas were greater than those in nitrogen-rich gas. The result indicated that adjusting the concentrations of nitrogen and oxygen could control the intensity of the electron emission and the properties of the 1-butanol polymers.

The analyses of stability of the 1-butanol polymer, the ratio of nitrogen fixed in the polymer, and the length of electron emission for forming the stable polymer revealed nitrogen to be a key species for forming stable 3-D bridge structures and producing the 1-butanol polymer. In contrast, oxygen did not contribute to forming the polymer. If anything, oxygen prevented the formation of the polymer or even decomposed the produced polymer. However, oxygen contributed to forming the more stable 1-butanol polymer by removing the unstable molecules from the polymer and enhancing the ratio of nitrogen in the polymer. In fact, the viscosity of the 1-butanol polymer increased as the ratio of nitrogen in the polymer increased after the longer electron emission in standard gas.

The FTIR analysis detected an intense C═O peak from the 1-butanol polymer formed in the standard atmosphere. In contrast, the C═O peak could not be detected from the polymer formed in the nitrogen-rich atmosphere. The selective formation of the peak in the standard atmosphere clearly demonstrated that the oxygen in the atmosphere was fixed in the polymer as C═O bonds instead of oxidation of O−H groups in alcohol.

The criteria of the ratio of nitrogen to oxygen for forming stable alcohol polymers and the components of the gases produced during the alcohol polymerization will be reported in the future.

Supporting Information Available: Differences in the surface of 1-butanol before and after the application of an electric potential in high-purity oxygen. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Schaller, R. D.; Lee, L. F.; Johnson, J. C.; Haber, L. H.; Saykally, R. J. *J. Phys. Chem. B* **2002**, *106*, 9496.

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(2) Sun, S.; Chong, K. S. L.; Leggett, G. J. *J. Am. Chem. Soc.* **2002**, *124*, 2414.

(3) Kunde, J.; Baumann, B.; Arlt, S.; Genoud, F. M. *Appl. Phys. Lett.* **2000**, *77*, 924.

(4) Zhou, D. S.; Xu, N.; Li, L.; Ji, G.; Xue, G. *J. Phys. Chem. B* **2003**, *107*, 2748.

(5) Levis, R. J.; Menkir, G. M.; Rabitz, H. *Science* **2001**, *292*, 709.

(6) Levis, R. J.; DeWitt, M. J. *J. Phys. Chem. A* **1999**, *103*, 6493.

(7) DeWitt, M. J.; Levis, R. J. *J. Chem. Phys.* **1999**, *110*, 11368.

(8) Teare, D. O. H.; Spanos, C. G.; Ridley, P.; Kinmond, E. J.; Roucoules, V.; Badyal, J. P. S. *Chem. Mater.* **2002**, *14*, 4566.

(9) Fu, G. D.; Kang, E. T.; Neoh, K. G. *J. Phys. Chem. B* **2003**, *107*, 13902.

(10) Hollahan, J. R.; Bell, A. T. *Techniques and Applications of Plasma Chemistry*; John Wiley & Sons: New York, 1974.

(11) Hubner, C. G.; Zumofen, G.; Renn, A.; Herrmann, A.; Mullen, K.; Basche, T. *Phys. Rev. Lett.* **2003**, *91*, 093903−1∼4.

(12) Hamerli, P.; Weigel, Th.; Groth, Th.; Paul, D. *Biomaterials* **2003**, *24*, 3989.

(13) Murray, P. T.; Shin, E. D. *Radiat. Phys. Chem.* **2003**, *68*, 221.

(14) Boenig, H. V,; Ed. *Advances in Low-Temperature Plasma Chemistry, Technology, Applications*; Technomic Publishing: Lancaster, PA, 1984.

(15) Matsuura, H.; Tanikawa, T.; Takaba, H.; Fujiwara, Y. *J. Phys. Chem. A* **2004**, *108*, 3235.

(16) Matsuura, H.; Tanikawa, T.; Takaba, H.; Fujiwara, Y. *J. Phys. Chem. B* **2004**, *108*, 17748.

(17) Matsuura, H.; Tanikawa, T.; Takaba, H.; Kokaji, S. *J. Phys. Chem. A* **2004**, *108*, 7099.

(18) Imai, I. *J Phys. Soc.* **1991**, *60*, 4100.

(19) Imai, I., Ed. *DENJIKIGAKU O KANNGAERU*; Saiensu-sya: Tokyo, 1990. English translation: *A New Approach to Electromagnetic Theory. Bull. Soc. Fr.-Jpn. Sci. Pures Appl., Num. Spec.* **1990**, *4*, 353.