Investigation of the Requirements for Plasma-Induced Polymerization of Alcohols

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We analyzed the requirements for plasma-induced alcohol polymerization by comparing the reactions of several types of aliphatic alcohols and alkanes. The experiments revealed that alcohol polymerization requires the fixation of atmospheric nitrogen into alcohol. The OH group in alcohol physically contributes to initiate the airborne plasma reactions with its permittivity. However, the group chemically works to inhibit the fixation of nitrogen and successive polymerization of alcohols. Our study demonstrates that the ratio of OH groups per weight percent of each molecule decides the feasibility of the polymerization and the properties of the polymers.

Introduction

We previously produced an alcohol-based hydrogen-storing polymer using a plasma-induced reaction.[1] Hydrogen atoms in alcohol were dissociated during this reaction, and hydrogen was stored as ions in the polymer. Nitrogen molecules in air were also dissociated and fixed in the polymer.[2] These simultaneous reactions are considered a replacement of hydrogen with nitrogen.

This plasma-induced reaction was initiated by electron emission onto the liquid alcohol surface.[1,2] The emitted electrons collided with the alcohol molecules and were attracted to the electrode due to the molecules' permittivity. The collision decomposed the alcohol molecules and produced positive and negative ions, which were immediately attracted and neutralized at the electrically opposite electrodes to form an alcohol polymer.[1,2] 1-Butanol was primarily used to analyze the alcohol polymerization as a function of the frequency and magnitude of the applied electric potential.[1,2] However, the requirements and the mechanisms of the alcohol polymerization were not specified.

In this paper, several aliphatic alcohols, such as methanol, butanol, and pentanol, and alkanes, such as pentane and hexane, were used to investigate the mechanisms and requirements for plasma-induced polymerizations. The comparison of the reactions between aliphatic alcohols and alkanes revealed the physical role of the OH group with its permittivity for initiating airborne plasma reactions. The comparison of the reactions between the alcohols demonstrated the chemical role of theOH group[3] in activating alcohol hydrolysis and preventing the fixation of nitrogen and successive polymerization.

Apparatus

Figure 1 depicts a microscale reactor used to observe a plasma-induced polymerization achieved by electron emission
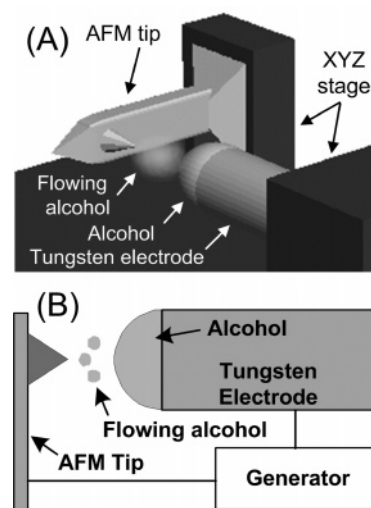

Figure 1. Apparatus for exciting and polymerizing alcohol molecules using electron emission: (A) 3D image of the alcohol polymerization apparatus; (B) 2D image of the alcohol polymerization apparatus.

in an intense electric field. The microscale reactor is suitable for directly observing delicate polymerization reactions.

The core elements of this apparatus are a negative electrode consisting of an AFM tip with a radius of 20 nm, a positive tungsten electrode with a diameter of 1 mm, and organic solutions placed on the side of the positive tungsten electrode. One microliter of solution was supplied continuously to the side of the tungsten electrode from a glass tube with an inner diameter of 0.1 mm to form a hemispherical, quasi-positive electrode, as illustrated in Figure 1. The distance between the AFM tip and the edge of the tungsten electrode was set to 0.4 mm, and the surface of the alcohol was adjusted to 55 μm from the AFM tip. The AFM tip and the tungsten electrode were mounted on *XYZ* stages for accurately adjusting their distances. A generator was connected between the AFM tip and the tungsten electrode to apply the electric potential. A pulsed electric potential of 0.8 kV was applied between the electrodes

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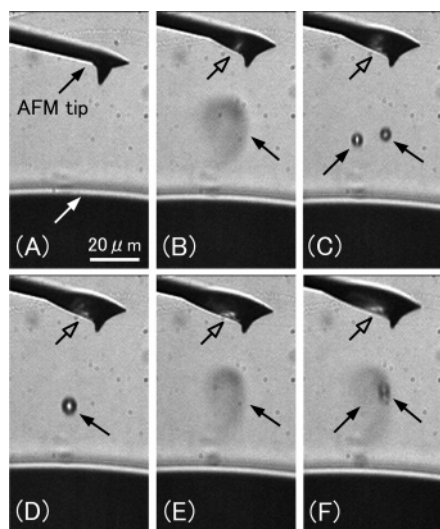[§] Shibaura Institute of Technology.

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Figure 2. Dynamics of alcohol polymerization. Part A depicts an AFM tip (black arrow) as a negative electrode and the surface of alcohol (white arrow) placed on the positive tungsten electrode. When an electric potential of 0.8 kV at 15 kHz was applied, a nanoscale mist appeared between the AFM tip and the alcohol surface (part B, black arrow). The mist in part B condensed to the two microscale droplets shown in part C (black arrows). The two droplets in part C then merged into the larger microscale droplet shown in part D (black arrow). The large microscale droplet in part D collapsed into a nanoscale mist, as shown by the black arrow in part E. The nanoscale mist in part E condensed again into the microscale droplet(s) shown in part F (black arrow). The cycle of appearance and disappearance of the mist and droplets was sustained while the 0.8 kV at 15 kHz electric potential was applied. During this cycle, some portion of the mist and/or droplets was transferred to the AFM tip and adhered to it. The adhering material is indicated by white arrows from parts B–F. These reactions were observed when an electron emission of 28 μA was introduced from the AFM tip to the surface of alcohol. The influence of the electron charge can be observed in the reaction dynamics.

at a frequency of 15 kHz to generate electron emission. An optical microscope was mounted to observe the dynamics of liquid polymerization. The experiments were conducted in air at 26 °C and 50% humidity. The AFM tip consisted of a Au-coated silicon tip (DF-20, SII). The solutions were 99.5% pure (Wako Pure Chemicals).

The fabrication of a positive electrode covered with a liquid is a unique feature of the apparatus. The design of the apparatus played an important role in generating the flowing molecular current (Figure 1) and gentle emission of electrons into the current. The design also contributed to avoid uncontrolled discharges or combustion during the plasma-induced airborne reactions.

Dynamics of Alcohol Polymerization

Figure 2 depicts the interaction between the emitted electrons and alcohol molecules. Figure 2A presents an optical image of the AFM tip and the surface of the solution without an electric potential between the electrodes. Nano- and microscale mist alternatively appeared between the AFM tip and the surface of the dielectric solution when an electric potential of 0.8 kV–15 kHz was applied between the electrodes (Figure 2B–F, black arrows).

The phenomenon was only observed when an average electric current of 2 μA was detected with an input current of 28 μA. This clearly demonstrated that a unique dynamic in alcohol polymerization was related to the consumption of 26 μA of electrons during the airborne reactions (Figure 2, black arrows).
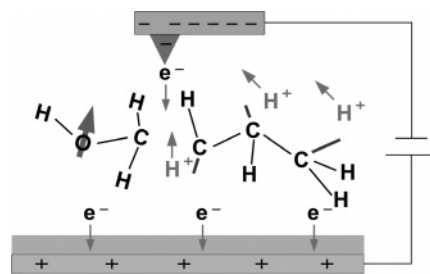

Figure 3. Model of the molecular current and the dissociation of molecules. The asymmetrical electric field between the sharpened negative electrode and the positive electrode electrically attracted dielectric molecules toward the smaller electrode. The tip simultaneously emitted electrons toward the attracted molecules and dissociated the molecules during their collision in air.

The mist in Figure 2B condensed into two droplets, as indicated in Figure 2C, and the droplets then formed one large droplet, as signified by the black arrow in Figure 2D. This large droplet then transformed into the mist shown in Figure 2E. Figure 2F depicts the moment the mist in Figure 2E condensed back into a droplet.

The unstable dynamics of the liquid can be explained as follows. The asymmetrical electric field around the AFM tip electrically attracted the volatile alcohol molecules with their permittivity from the liquid surface to the tip.[4–6] The intense electric field around the AFM tip simultaneously generated electron emission toward the attracted molecules. Their collision dissociated the alcohol molecules into positive and negative ions (radicals). Some dissociated positive and negative ions (radicals) were immediately attracted and neutralized at the electrically opposite electrodes to form an alcohol polymer. Gradual increases of the volume of the compounds adhering to the AFM tip, indicated by the white arrows in Figure 2, represent condensation of the attracted positive ions. Other ions (radicals) interact with the electric field between the electrodes and cause unique liquid dynamics, as indicated by the black arrows in Figure 2.

These unstable liquid dynamics combined with the consumption of the applied electron emission suggest that the mists and droplets in Figure 2 are in electrically unstable states. This may be due to the charge of the electrons and dissociated ions. The unusual alternating transitions between mists and droplets support this suggestion.

The dissociation process of alcohol molecules[7–9] and successive polymerization, as outlined in Figure 2, is illustrated in Figure 3. The intense electric field near the AFM tip generated an electron emission (Figure 3, arrows) and simultaneously attracted the dielectric alcohol molecules toward the tip through a polarization interaction. The permittivity of OH groups in the alcohol molecules (Figure 3, large arrow) contributed to the formation of the molecular current toward the tip.

The electron emission into the molecular current directed toward the tip caused their collision and successive dissociation of the molecules (Figure 3). The dissociation of the molecules led to the production of various positive and negative ions[7–9] that immediately migrated toward the negative and positive electrodes. The alcohol polymer formed after electrical neutralization of these ions at the electrically opposite electrodes.

Feasibility of Plasma-Induced Polymerization

The influence of the molecular properties on plasma-induced polymerization was investigated. The important physical constants for polymerization, including molecular weight, boiling point, and permittivity, are listed in Table 1. The investigation

TABLE 1: Requirements for Polymerization[a]

Components	Properties	Polymerization	Molecular Weight	Boiling Point $\left(-\frac{Room}{Temp.}\right)$		Permittivity
A	Methanol	△	32.04	64.7	(38.7)	32.6
	Ethanol	△	46.07	78.3	(52.3)	24.55
B	1−Propanol	○	60.1	97.15	(71.15)	20.33
	1−Buthanol	◎	74.12	117.3	(91.3)	17.51
	1−Pentanol	◎	88.15	138	(112)	13.9
C	Pentan	✕	72.15	36.1	(10.1)	—
	Hexan	✕	86.18	68.74	(42.47)	1.8

[a] The molecules used in this analysis were classified as groups A, B, and C according to the feasibility of polymerization. The feasibility of the polymerization of these molecules was represented as a circle, a triangle, or a cross. A circle means that the molecule (1-propanol) was formed into an alcohol polymer. A double circle indicates that the molecules (1-butanol and 1-pentanol) were formed into alcohol polymers in a shorter time than those indicated by a circle. A triangle indicates that the molecules (methanol and ethanol) could hardly form detectable amounts of polymers. A cross indicates that the molecules never formed alcohol polymers in this research. Some properties of these molecules (molecular weight, boiling point, and permittivity) related to the alcohol polymerization are also listed in the table.

TABLE 2: Weight Percent of Components in Alcohol Polymers[a]

alcohol polymer	emission time (s)	carbon	oxygen	nitrogen
1-propanol polymer	45	56	11.4	32.6
1-butanol polymer	30	63.8	13.6	22.6
1-pentanol polymer	5	66.8	16	17.3

[a] The length of electron emission for synthesizing the molecules in group B (Table 1) and the weight percents of carbon, oxygen, and nitrogen in the polymers in group B are listed in Table 2. The weight percents of these components were measured with EPMA (Figure 4).

was conducted using several types of aliphatic alcohols and alkanes (Table 1). Compounds with the simplest molecular structure, a straight-chain structure, were selected to analyze the requirements of plasma-induced polymerization.

The compounds were classified as groups A, B, and C according to the feasibility of polymerization. Group A included methanol and ethanol, which were difficult to polymerize on the AFM tip. Group B consisted of 1-propanol, 1-butanol, and 1-pentanol, which were easily polymerized on the tip, as indicated by the white arrows in Figure 2. Observations of the polymerization of 1-propanol confirmed that some portion of the adhering compound evaporated quickly, and it took a relatively long time (45 s, Table 2) to compose the same amounts of compounds as 1-butanol or 1-pentanol. Group C contained pentane and hexane, which did not form visible airborne reactions or electrically attracted adhered compounds (Figure 2, white arrows) and could not be polymerized at all. The feasibilities of polymerization are represented by a circle, a triangle, and a cross in Table 1.

Components and Structure of the Alcohol Polymers

The weight percents of the components in the alcohol polymers in group B (Table 1) were measured with electron probe microanalysis (EPMA). Table 2 and Figure 4 present the weight percents of carbon, nitrogen, and oxygen in the alcohol polymers made from 1-propanol, 1-butanol, and 1-pentanol. Polymerization was conducted until the same amounts of polymers were composed on the AFM tip (Figure 2, white arrows).
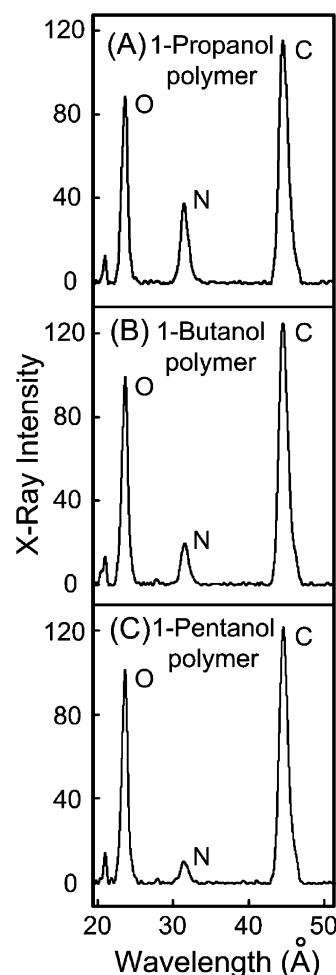

Figure 4. EPMA signal of alcohol polymers. Signals A, B, and C represent the weight percent of the polymers in Table 2 and correspond to the IR data of the polymers in Figure 5.

The lengths of emission times in Table 2 clearly indicate that an alcohol with a lower molecular weight and lower boiling point, such as 1-propanol, takes longer to compose the same amount of alcohol polymer than an alcohol with a greater molecular weight. In contrast, a heavier alcohol with a higher boiling point, such as 1-pentanol, quickly (within 5 s) composed the same amount of polymer as a lighter alcohol. These results demonstrate that heavier molecules with higher boiling points are able to immediately polymerize the same amount of polymer as lighter molecules with lower boiling points. However, the components of the alcohol polymers were very different, as indicated in Table 2.

An analysis of the transition of the molecular weights from alcohol to the corresponding alcohol polymer yielded intriguing results. The molecular weights of carbon are 60 in 1-propanol, 64.9 in 1-butanol, and 68.2 in 1-pentanol. A comparison of these values with those of the corresponding alcohol polymers in Table 2 reveals that the weight percent of carbon was not drastically decreased during polymerization.

The molecular weights of oxygen are 26.7 in 1-propanol, 21.6 in 1-butanol, and 18.2 in 1-pentanol. A comparison of these values with those of the corresponding alcohol polymers in Table 2 reveals that the weight percents of oxygen decreased depending on the length of electron emission. The alcohol polymer that underwent longer electron emission was decreased by a greater weight percent of oxygen. This indicated that some oxygen in the OH group was removed and that oxygen in the
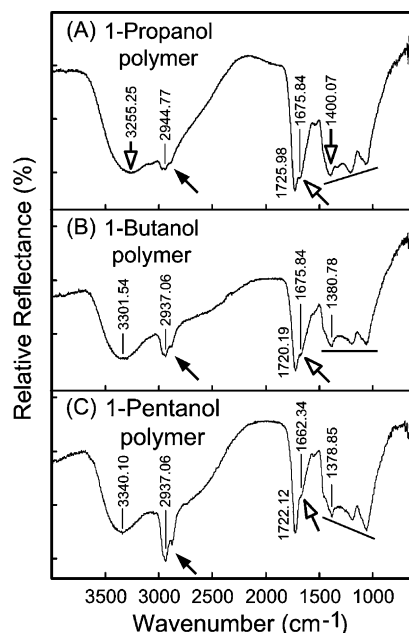
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Figure 5. FTIR spectra of alcohol polymers: (A) 1-propanol polymer after 45 s of electron emission; (B) 1-butanol polymer after 30 s of electron emission; (C) 1-pentanol polymer after 5 s of electron emission.

air might not be fixed in the alcohol polymers during plasma-induced polymerization.

These results differ from other types of plasma-induced gaseous reactions because oxygen in the atmosphere is often fixed in plasma-induced products.[10−11] Therefore, liquid alcohol polymerization in air might be based on processes that differ from other plasma-induced gaseous reactions.

The detection of nitrogen in the EPMA indicated that the nitrogen in air was fixed in the alcohol polymers during the plasma-induced reactions. Our experimental results demonstrated that a longer electron emission drastically increased the weight percent of the nitrogen in the alcohol polymers. This is evident when comparing the weight percent of the fixed nitrogen in the 1-propanol polymer and 1-pentanol polymers in Table 2 and Figure 4.

The observation of the polymerization process of 1-propanol indicates that the concentration of the fixed nitrogen should be enhanced during the continuous composition and simultaneous evaporation of the 1-propanol polymer on the AFM tip. This suggests that the stability of the alcohol polymer should be enhanced as the concentration of nitrogen is increased. In contrast, polymerization of 1-pentanol with a greater molecular weight and a higher boiling point was quickly achieved. However, the amounts of fixed nitrogen were much less than for the 1-propanol polymer, as indicated in Table 2 and Figure 4. These results confirm that the combination of emission time and the type of alcohol can control the composition of an alcohol polymer.

The properties and structure of the alcohol polymers were analyzed using the microscopic-FTIR spectra. Figure 5 presents the IR spectra of the alcohol polymers of 1-propanol, 1-butanol, and 1-pentanol (corresponding to those in Table 2 and Figure 4).

It is interesting to analyze the transitions of the IR spectra in Figure 5 from the standpoints of emission time and components of the alcohol polymers. The IR peaks become sharper from part A to part C of Figure 5. The sharp IR peaks in the 1-pentanol polymer (Figure 5C) indicate that the 1-pentanol was not adequately polymerized; the structure of the 1-pentanol

polymer remains as the structure of the corresponding alcohol.[12−14] In contrast, the broad IR peaks in the 1-propanol polymer (Figure 5A) indicate that the 1-propanol was adequately polymerized and the formation of a 3D bridge structure was expected.[2,12−14]

The formation of these different IR spectra should be based on the length of electron emission, as indicated in Table 2. A longer electron emission with adequate kinetic energy decomposed both 1-propanol and nitrogen in air and composed a nitrogen-rich 1-propanol polymer (Figure 5A). The fixation of nitrogen at the molecular level could be observed in the simultaneous formations of 3255, 1675, and 1400 (cm^{-1}) peaks in the 1-propanol polymer[2,12−14] (Figure 5A, white arrows).

The intensity increase of the 1675 peaks from part C to part A of Figure 5 with respect to the 1725 peaks, in addition to the peak shift of OH stretching from 3340 (Figure 5C) and 3301 (Figure 5B) to 3255 in Figure 5A, supports the theory that longer electron emission enhances the concentration of fixed nitrogen in the polymer.[12−14] Fixed nitrogen in the alcohol polymer evidently contributes to composing stable 3D bridge structures,[2] since the viscosity of the 1-propanol polymer was ultimately greater than the other alcohol polymers.

In contrast, those peaks were not clearly observed in the 1-butanol polymer (Figure 5B) or the 1-pentanol polymer (Figure 5C) due to the shorter emission time of the electrons and the resulting inadequate fixation of nitrogen in these polymers.

The effect of a longer electron emission on the decomposition of alcohol molecules could also be observed in the various IR transitions. The drastic decrease of the 2944 peaks in Figure 5A (black arrow) indicates that the structure (CH$_2$ and CH$_3$ stretching) of the propanol was more greatly decomposed compared to butanol (Figure 5B) and pentanol[2,12−14] (Figure 5C).

The transitions of the peak structure around 1000−1500 (cm^{-1}) in Figure 5 also indicate the degree of polymerization caused by the length of electron emission time. The black lines under the peaks in each part of the figure represent the angles of the peak tops. The angle of the nitrogen-rich polymer after a longer electron emission in Figure 5A rises to the right. However, the angle becomes flat for the 1-butanol polymer (Figure 5B), and the angle of the nitrogen-poor polymer becomes downward to the right, as illustrated in Figure 5C.

Requirements for Plasma-Induced Polymerization

Figures 4 and 5 clearly demonstrated that the fixation of nitrogen into the polymer is a requirement for composing a stable alcohol polymer. The comparison of the viscosity with palpations also demonstrated that the more the nitrogen was fixed into the polymer, the more the polymer gained viscosity and became stable: the 1-propanol polymer containing 32.6 wt % nitrogen was more viscose and stable than the 1-pentanol polymer containing 12.3 wt % nitrogen.

Fixing nitrogen into the polymer requires the molecular current from the liquid surface to the AFM tip, the airborne plasma reaction (Figure 2, black arrows), and the successive electrical neutralization of the compound at the tip (Figure 2, white arrows).

The comparison of polymerization feasibility among groups A, B, and C in Table 1 indicated that the physical and chemical functions of the OH group[3] played critical roles for inducing the airborne plasma reaction and composing the nitrogen-fixed stable polymers.

The physical role of the OH group[3] is identified from the comparison of the plasma reaction between groups B and C in Table 2. During polymerization of group B, the alcohol current from the liquid surface to the AFM tip and the successive airborne plasma reaction between the electrodes were observed (Figure 2). However, these current and airborne reactions were never observed during the polymerization of group C.

The OH group is the only structural difference of the molecules between groups B and C. The fact that the airborne plasma reaction between the electrodes (Figure 2) was only observed in group B experiments strongly supported the concept that the group B molecules with OH groups interacted with the electric field permittivity and were electrically attracted toward the AFM tip. In contrast, the group C molecules without an OH group could not sufficiently interact with the electric field and were not electrically attracted toward the AFM tip.

These results indicated that the OH group played a critical role in initiating the plasma-induced polymerization. The permittivity of the OH group interacted with the asymmetrical electric field in Figure 2 and caused the molecular flow from the liquid surface to the AFM tip. The molecular flow collided with electrons emitted from the AFM tip and caused the airborne plasma reactions between the electrodes (Figure 2).

Although hexane has a weak permittivity (1.8), the electrical interaction might not be sufficient to arrive at the appropriate reaction area around the AFM tip in air. The intense electron emission toward the hexane on the positive electrode (Figure 1) might also prevent the arrival of molecules around the AFM tip.

The chemical role of the OH group[3] could be recognized from the comparison of the plasma reactions between groups A and B (Table 2).

During these experiments, the airborne plasma reaction (Figure 2, black arrows) was observed. This is reasonable since both groups of molecules contain an OH group in the molecule and could be attracted to the AFM tip through their permittivity. However, the reaction time for composing the same volume of compounds (Figure 2, white arrows) was much different. The molecules in group A took more time than those in group B. This suggests that the differences of these reactions are not caused by physical effects but caused by chemical effects.

The molecules in groups A and B differ structurally in the ratio of OH groups per molecular weight of each molecule. The ratio in group A is higher than that in group B. The experiments showed that the molecules in group A with more OH groups had more difficulty composing the same amount of polymers and took more time than those in group B. This clearly demonstrated that the OH group worked unfavorably for the polymer composition.

Since plasma-induced polymerization requires the fixation of nitrogen in the polymer during the airborne reaction, the existence of too many OH groups would prevent nitrogen fixation. The OH group in alcohol often hydrolyzes alcohol;[3] therefore, alcohol hydrolysis caused by too many OH groups might dominate the fixation of nitrogen during the airborne plasma reactions. The formation of C=O bonding (1720 cm^{-1}) in Figure 5 supports this assumption.

These analyses demonstrated that the OH group played an important role in plasma-induced polymerization. The OH group in the molecule physically contributed by interacting with the electric field with their permittivity, thus initiating airborne plasma reactions. However, the OH group in the molecule could inhibit nitrogen fixation; therefore, too many OH groups would prevent alcohol polymerization.

It is obvious that the OH group inside the alcohol contributes to the electrical interaction and subsequent airborne reactions. However, we cannot assume that the OH groups originated only from the alcohol effect of the airborne plasma reactions. Since the dissociation energy of H_2O (12.61 eV) is less than that of nitrogen (15.59 eV), there is a distinct possibility that the OH groups dissociated from H_2O molecules in air also affect the airborne plasma polymerizations.

The stability of the alcohol in air, which originated from the molecular weight or the boiling point of the alcohol, should also be related to the feasibility of polymerization. Alcohol polymerization is achieved by the following processes, as illustrated in Figure 3. The alcohol molecules are electrically attracted to the AFM tip and dissociated through the collisions with electrons emitted from the tip and adhering on the tip where they are electrically neutralized. If electron emission dissociated just part of the molecules and they kept their inherent properties, the alcohol with a greater molecular weight or a higher boiling point should be stable and have a greater likelihood to be polymerized on the AFM tip. The partially dissociated molecules arriving at the AFM tip require some time for electrical neutralization and the simultaneous fixation of nitrogen for the stable polymer.

The experimental results support this assumption: methanol and ethanol with smaller molecular weights were hardly polymerized, in all probability due to the quick evaporation of partially dissociated molecules. 1-Propanol also took a long time for polymerization, likely due to the continuous evaporation of the partially dissociated molecules. In contrast, 1-butanol and 1-pentanol were easily polymerized because they had sufficient stability on the AFM tip for the electrical neutralization and simultaneous fixation of nitrogen.

However, the 1-propanol polymer fixed more nitrogen than the 1-butanol or 1-pentanol polymer in the same volume (Table 2). This could be because the concentration of fixed nitrogen was increased during the continuous evaporation of attracted ions and fixation of the stable nitrogen compound during the lengthy period of time (45 s).

Summary

We investigated the mechanisms of alcohol polymerization by directly observing the reactions with an optical microscope combined with the EPMA and the FTIR analysis. These analyses demonstrated that the alcohol polymerization required the fixation of atmospheric nitrogen. The fixation of nitrogen required the molecular current from the liquid surface to the AFM tip, the airborne plasma reaction, and the successive electrical neutralization of the compound at the tip.

An appropriate amount of OH groups in alcohol is necessary for interacting with the electric field and successive polymerization at the AFM tip. However, the reactive OH group would cause the hydrolysis of alcohol, and too many OH groups prevent the fixation of nitrogen into alcohol and subsequent polymerizations. The molecular weight of alcohol would also be related to the feasibility of the fixation of nitrogen and the resulting composition of stable polymers.

The alcohol polymerization in the closed system filled with oxygen or nitrogen at the various temperatures and humidity will be reported in the next paper.

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