

Novel Method of Preparing Ag–Hg Alloy on Polyacrylamide Films and Their Structure

JIUNN YIH LEE, HISASHI TANAKA, HIDEO TAKEZOE, ATSUO FUKUDA, and EIICHI KUZE, *Tokyo Institute of Technology, Department of Textile and Polymeric Materials, O-okayama, Meguro-ku, Tokyo 152, Japan*, and HIROSHI IWANAGA, *Nagasaki University, Faculty of Liberal Arts, Bunkyo-machi, Nagasaki 852, Japan*

Synopsis

A novel method is proposed of preparing thin Ag–Hg alloy on PAAM film surface at room temperature: The film of interest is formed by holding PAAM aqueous solution with AgNO_3 in Hg-saturated atmosphere. Two kinds of films, one of which is a conductor and the other an insulator, can be selectively formed with pH-controlled PAAM solution by ammonia. The conducting surface is assigned to the α phase of Ag–Hg alloy by means of X-ray analysis. Potentiometric titration and IR spectral studies suggest the existence of PAAM– Ag^+ complexes. On the basis of their structure and the oxidation and reduction potential of Ag^+ and Hg^{2+} , the mechanism of film formation is also discussed.

INTRODUCTION

It is well known that an aqueous solution of poly(vinyl alcohol) forms a complex with Cu^{2+} .^{1,2} Such a formation of complexes sometimes gives rise to additional functions or improves the functional properties such as electric conductivity and photoconductivity in polymer films. Systematic investigation of complexes of water-soluble polymers with transition metals has been carried out for the past several years in this laboratory with successful results.^{3–6} Among various combinations of polymers such as poly(vinyl alcohol), polyacrylamide, poly(vinyl pyrrolidone), poly(acrylic acid), and poly(ethylene glycol) (hereinafter abbreviated to PVA, PAAM, PVPr, PAAc, and PEG) and transition metal salts, it has been found that photoconductivity appears in several combinations, PVA– CuCl_2 , PVA– CuBr_2 , and PVA– FeCl_3 ,^{5,6} though the electric conductivity itself is not improved so much. In addition, a variety of electron spin resonance (ESR) signals as a function of the molar ratio of OH^- and Cu^{2+} , $[\text{OH}^-]/[\text{Cu}^{2+}]$, showed that the structure of the complex is not as simple as has been considered so far but is manifold corresponding to the value of $[\text{OH}^-]/[\text{Cu}^{2+}]$.³

In the process of the above-mentioned investigation, we found a method of preparing a thin metallic film on a polymer substrate. This is possible only for a combination of PAAM and AgNO_3 ; Ag–Hg alloy is formed over the PAAM film by leaving a cast aqueous solution of PAAM and AgNO_3 in Hg atmosphere. The investigation was motivated by a wish to realize a model system of Ginzburg's superconducting materials, which is a 2-dimensional metallic thin film on dielectric materials. Although the film obtained does not give rise to any noticeable superconducting properties, we report here the process of film formation and

TABLE I
List of PAAM Purchased from Several Companies

| Manufacturer | Polymer | | Molecular weight (M_w) | pH |
|-------------------------------------|------------------------------|-----|----------------------------|------|
| Sumitomo Chemical Co., Ltd. | Sumitex Resin A-1 | 10% | 545×10^3 | 8.23 |
| | Sumitex Resin A-1 Special | 10% | 407×10^3 | 5.92 |
| Tokyo Kasei Kogyo Co., Ltd. | Acrylamide (polymer) | 10% | 594×10^3 | 4.65 |
| Nakarai Chemicals, Ltd. | Acrylamide (polymer) | 10% | 663×10^3 | 6.82 |
| Wako Pure Chemical Industries, Ltd. | Acrylamide (polymer) | 10% | 566×10^3 | 8.08 |

the structural characterization by X-ray analysis since the alloy is prepared with a novel method and is well characterized.

EXPERIMENTAL AND DISCUSSION

Characterization of PAAM. As mentioned above, the alloy of interest can be formed only on a PAAM film. Moreover, the appearance and the structure of the films formed are very sensitive to PAAM used. So we first describe the characterization of PAAM by means of gel permeation chromatography and elementary analysis. Table I shows pH and average molecular weight (M_w) of PAAM purchased from several companies. Both the pH and the M_w distribute over a rather wide range. Mainly we used Sumitex Resin A-1 after refinement in a mixed solution of methanol and toluene with a mixing ratio of 3:1. The refining removes lower molecular weight polymers and decreases the pH as shown in Table II. It is well known that PAAM produces ammonia by hydrolysis. Actually the existence of ammonia was confirmed in the mixture of methanol and toluene used for refining. Thus ammonia mainly dominates the pH of an aqueous solution of PAAM. The refined PAAM after removing alkaline impurities is rather acid since PAAM in part dissociates protons, and, moreover, there exists PAAc taken in during the polymerization of PAAM or produced by hydrolyzing PAAM. The existence of PAAc is seen in the result of elementary analysis as shown in Table III: Comparing with the calculated values for ideal PAAM, the PAAM used contains excess oxygen atoms and less nitrogen atoms.

Formation of Polymer-Metal Complex. The formation of the Ag-Hg alloy of interest has been so far restricted to the case of PAAM and AgNO_3 . To investigate the correlation between the film formation and the existence of complex structure, potentiometric titrations were carried out for aqueous solutions of PAAM with AgNO_3 or $\text{Cu}(\text{NO}_3)_2$. Figure 1 shows the results for PAAM solutions with AgNO_3 before and after refining [(a) and (b), respectively]. The results of the solutions with $\text{Cu}(\text{NO}_3)_2$ [(c) and (d), respectively] are also shown for

TABLE II
Variation in pH and Molecular Weight of PAAM by Refining

| | M_w | pH |
|----------------|-------------------|------|
| Unrefined PAAM | 545×10^3 | 8.23 |
| Refined PAAM | 593×10^3 | 4.50 |

TABLE III
 Result of Elementary Analysis for Sumitex Resin A-1

| | H (%) | C (%) | N (%) | O (%) | Total (%) | |
|-------------------|-------|-------|-------|-------|-----------|----------------------------|
| PAAm calcd | 7.09 | 50.69 | 19.71 | 22.51 | 100.00 | $H_5C_3N_1O_1$ |
| Sumitex Resin A-1 | 7.60 | 46.98 | 17.20 | 27.61 | 99.39 | $H_{5.8}C_3N_{0.9}O_{1.3}$ |

reference. In the figure, F_1 defines the ratio of the molar concentration of metal ion to that of monomeric unit of PAAm, $[M^{n+}]/[MU]$. The four figures (a)–(d) show similar behavior; a sharp increase in pH by titrating small amount of NaOH and the existence of a buffer region except the case of $F_1 = 0$. The sharp increase is ascribed to neutralization of dissociated H^+ from PAAm. The existence of the buffer region only for PAAm with $AgNO_3$ or $Cu(NO_3)_2$ suggests that Ag^+ or Cu^{2+} forms complexes with PAAm and the complexes have dissociable H^+ . In Figures 1(a) and (b), the neutralization point locates around $[OH^-]/[MU] = 0.5$ and 1 for the solution of $F_1 = 0.5$ and 1, respectively, leading to the conclusion that one proton per one Ag^+ ion is dissociated. The comparison between (a) and (b) or (c) and (d) shows that the refining of PAAm does not give significant differences in complex formation, although the buffer region in (a) is a little narrower than that in (b). It is also concluded by comparing (a) and (c) or (b) and (d), that PAAm- Cu^{2+} has a higher equilibrium constant than PAAm- Ag^+ . Thus PAAm forms a complex with Ag^+ as well as Cu^{2+} , though PAAm- Ag^+ is less stable than PAAm- Cu^{2+} .

To confirm the complex formation and, moreover, to investigate the structure of the complex, IR spectra were measured for films cast from PAAm aqueous solution with various concentration of $AgNO_3$. In Figure 2 are shown the IR spectra for refined PAAm films with $AgNO_3$ of $F_1 = 0, 0.1, 0.2,$ and 0.5 . The

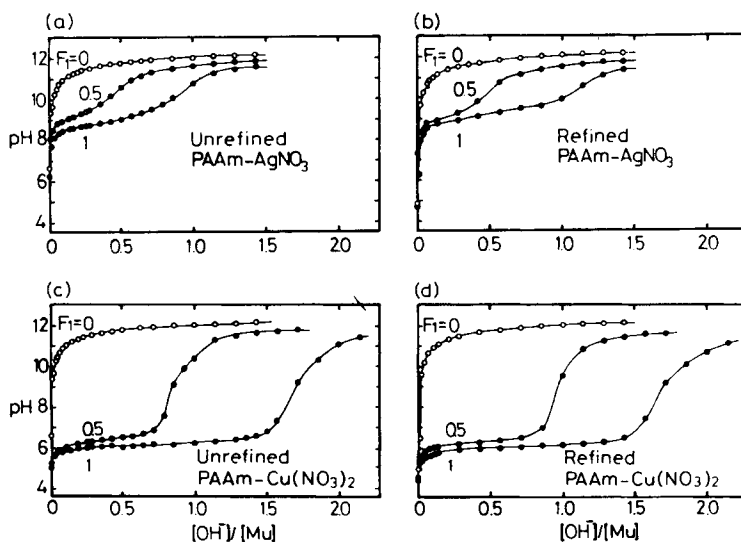


Fig. 1. Potentiometric titration curves for 0.014M PAAm aqueous solution with $AgNO_3$ [(a) and (b)] or $Cu(NO_3)_2$ [(c) and (d)] of three different F_1 values.

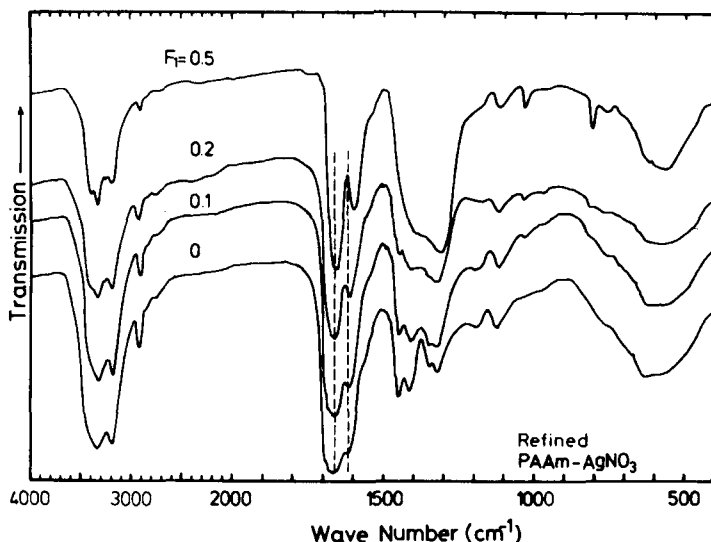


Fig. 2. Infrared absorption spectra of refined PAAm-AgNO₃ films with different F_1 .

results for the PAAm films without refining are essentially the same as those for the refined PAAm. It is clear that there appear systematic changes in the spectra with F_1 . Some of them are attributed to the vibrational modes of NO₃: a sharp peak at 810 cm⁻¹ and a broad peak around 1400 cm⁻¹. It should be noticed that a peak due to the N—H bending mode at 1620 cm⁻¹ shifts to shorter wave number side with increasing F_1 . Another spectral change is also observed in the region between 3000 and 3500 cm⁻¹, where two peaks are due to the N—H asymmetric stretching mode and the N—H symmetric stretching mode. Thus the vibrational modes originating from the N—H bond are affected by adding AgNO₃ to PAAm. Therefore, it is confirmed that PAAm and Ag⁺ ion form a complex as shown by titration curves, and it is suggested that Ag⁺ ion is coordinated by the amino group of a PAAm chain. This conclusion is consistent with the general knowledge⁷ that the coordinate bond for soft acid Ag⁺ is more stable toward nitrogen rather than oxygen even if oxygen is ionized. Moreover, protons are not dissociated from the NH₂ in PAAm when Ag⁺ ion is coordinated. This is clear from the fact that the pH does not change by adding AgNO₃ to refined PAAm as shown in Figure 3, where an initial decrease in unrefined PAAm may be attributed to the reaction such as $\text{Ag}^+ + 2\text{NH}_4^+ \rightarrow [\text{Ag}(\text{NH}_3)_2]^+ + 2\text{H}^+$.

We now discuss the structure of PAAm-Ag⁺. The titration studies carried out for solutions of PVA, PAAm, and PVPr with CuCl₂ indicate the existence of a buffer region even in PVPr which itself has no dissociable protons.³ Therefore, it has been concluded that the remaining two ligand sites of coordinated Cu²⁺ by a polymer chain are occupied by water molecules. These water molecules are responsible for the buffer region in a potentiometric titration curve obtained for solutions of PVA, PAAm, and PVPr with CuCl₂. Since the titration curve is quite similar to the one for PAAm-Ag⁺ in Figure 1, we conclude that the remaining ligand of Ag⁺ ion coordinated to nitrogen in PAAm is a water molecule. Although the ESR spectra have not been obtained for the case of Ag⁺ ion having no unpaired spin, the conclusion does not contradict any experimental results obtained.

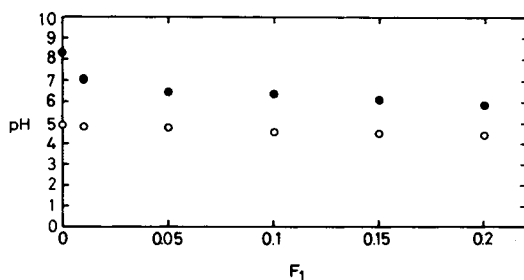


Fig. 3. Plot of pH vs. F_1 for unrefined (●) and refined (○) PAAm.

Preparation of Ag-Hg Alloy on PAAm Film. The polymers used are listed in Table I and were sometimes refined in a mixed solution of methanol and toluene with a mixing ratio of 3:1. The refining decreases the pH as mentioned above, resulting in a remarkable effect on characteristics of the film formed. No purification was performed for AgNO_3 and Hg.

Films were produced as follows. An aqueous solution of PAAm of 5 wt % was prepared, and AgNO_3 was added up to the concentration of $F_1 = 0.1$. The mixture was held overnight at room temperature after stirring for several hours. Then the solution was cast on to teflon sheet and left in an Hg-saturated atmosphere for about a week. The procedure was carried out in a box kept at 30°C as illustrated in Figure 4. It was observed that a thin metallic film was formed on the polymer surface. By drying for about several days in a dry box with silica gel, the final product of interest was obtained.

Characteristics of the Film. Before describing the result analyzed by means of X-ray diffraction, we summarize the apparent characteristics of the films. The films produced are roughly classified into two types as shown in Figure 5. The surface of the left one (hereinafter called A) in the figure is whitish gray and is conductive. The right one (B) has a smooth and glossy surface of metallic luster but is an insulator. The reverse sides of both films appear blackish, although the bases are transparent polymer. In most of this work, Sumitex Resin A-1 was

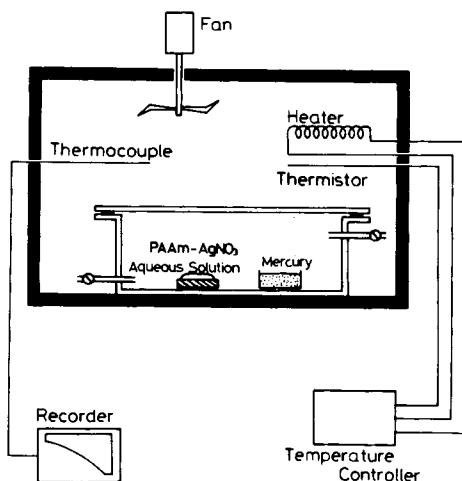


Fig. 4. Schematic illustration of reaction box for preparing films.

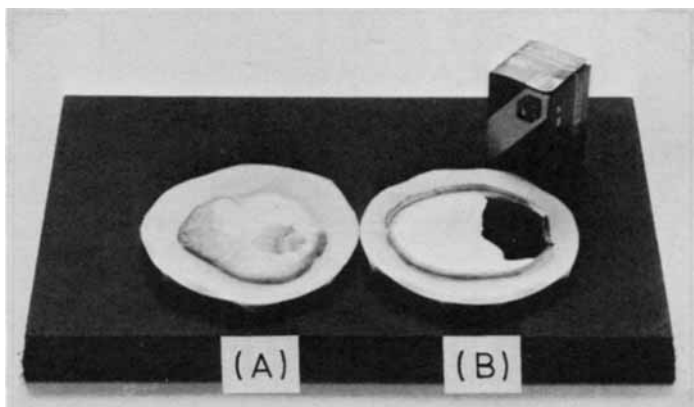


Fig. 5. Photographs of two different films formed with use of refined (A) and unrefined (B) PAAM.

used. Using the refined and the unrefined PAAM, we can produce the films A and B, respectively. Film B tends to become film A if it is kept in an Hg-saturated atmosphere much longer. The unrefined other polymers from different manufacturers, Tokyo Kasei Kogyo, Ltd., and Nakarai Chemical, Ltd., give rise to film A modified by slight mixture of the B type film. The refined ones give rise to various types of film which cannot be classified as either film A or B. Therefore, the films produced from PAAM except for Sumitex Resin A-1 will not be referred any more in this paper. From scanning electron microscopy, the thickness of the overall film A is about $100\ \mu\text{m}$ and that of the alloy film is less than a few microns though it is very hard to observe the boundary to the polymer. The conductivity is estimated to be about $10^5\ \Omega^{-1}\cdot\text{cm}^{-1}$, assuming the thickness of $1\ \mu\text{m}$.

The results for the refined and the unrefined Sumitex Resin A-1 suggest that the pH of an aqueous solution of PAAM plays an important role in determining the type of film produced. As mentioned above, the pH of PAAM solution seems to be governed by ammonia. Therefore, we prepared films from pH-controlled PAAM solution by ammonia to clarify the relation between the pH and the characteristics of films. Two kinds of pH-controlled PAAM solutions were used, i.e., refined PAAM solutions with ammonia and mixed solutions of unrefined and refined PAAM, leading to the same results. This fact supports the conclusion that the pH of PAAM solution is governed by ammonia. It was confirmed that, roughly speaking, the film A is produced by using PAAM solution of pH between 4.5 and 6 and the film B between 6 and 9.

X-Ray Analysis. To identify the thin film produced on the surface of PAAM film, we scraped off the product and observed its X-ray Debye-Scherrer rings. Figure 6 shows the results for the film A and pure Ag. Both Debye-Scherrer rings are essentially the same. Therefore, the film is found to be an Ag-rich α phase of fcc structure. The following differences should be observed in Figure 6. The rings at large angles are somewhat vague for the film A, suggesting that the film A consists of solid solution. Careful analysis of the rings leads to different lattice constants between film A and pure Ag, as expected by different distances between parallel planes shown in Table IV; the lattice constant of the film A has a sample dependence and is in the range 4.1–4.2 Å while that of pure

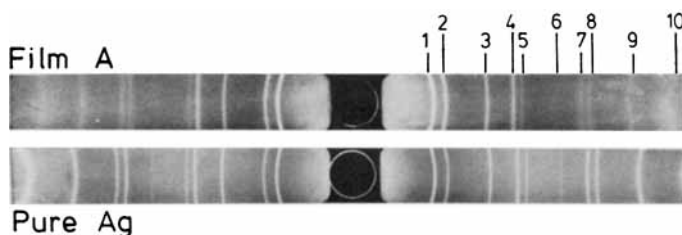


Fig. 6. X-ray Debye-Scherrer rings of the product on the surface of the film A and for pure Ag.

Ag is 4.086 Å, from which it is concluded that the film A consists of Ag-Hg alloy of α phase. The lattice constant, which, of course, increases with Hg content, can be controlled by the pH of PAAm solution. The full discussion of the effect of pH controlled by ammonia on characteristics of the film will be reported in a separate paper.

The film B is an insulator since the surface is covered with polymer. But the inner product is found to be also Ag-Hg alloy of α phase.

Mechanism of Film Formation. As mentioned above, Ag-Hg alloy is produced and spreads over polymer film surface by reacting the aqueous solution of PAAm and AgNO_3 in an Hg-saturated atmosphere. So far only the combination of PAAm and AgNO_3 is available for producing this film. And even PAAm solutions from different pH produce different types of film. Thus the formation is very sensitive to the polymer and metal used. Therefore, we restrict ourselves to discuss deposition of Ag atoms from PAAm- Ag^+ complexes. To create Ag atoms on the surface of PAAm- Ag^+ solution, Hg gas has to reduce Ag^+ ion. However, the oxidation-reduction potential of Hg^{2+} is a little lower than that of Ag^+ when hydrated, which seems to lead to the conclusion that Hg gas cannot reduce Ag^+ ions. But the equilibrium constant of Hg^{2+} ion is much larger than that of Ag^+ if their ligands are such as amine.⁸ Then the magnitudes of oxidation-reduction potentials of Ag^+ and Hg^{2+} in this environment are reversed and a reaction as shown in Figure 7 would take place. The assumption that Hg^{2+}

TABLE IV
Diffraction Angles (2θ) and Plane Distances (d) Corresponding to Lines Observed in X-Ray Analysis for Film A and Pure Ag^a

| Line | hkl | Film A experiment | | Pure Ag experiment | | Pure Ag reference | |
|------|---------|-------------------|-------|--------------------|-------|-------------------|-------|
| | | 2θ | d | 2θ | d | 2θ | d |
| 1 | 111 | 37.6 | 2.392 | 38.3 | 2.350 | 38.14 | 2.359 |
| 2 | 200 | 44.0 | 2.058 | 44.7 | 2.027 | 44.33 | 2.043 |
| 3 | 220 | 63.8 | 1.459 | 64.9 | 1.437 | 64.50 | 1.445 |
| 4 | 311 | 76.7 | 1.242 | 77.9 | 1.226 | 77.61 | 1.230 |
| 5 | 222 | 80.4 | 1.194 | 82.2 | 1.173 | 81.52 | 1.181 |
| 6 | 400 | 96.3 | 1.035 | 98.3 | 1.019 | 97.98 | 1.022 |
| 7 | 331 | 108.7 | 0.949 | 111.1 | 0.935 | 110.64 | 0.937 |
| 8 | 420 | 113.2 | 0.923 | 115.3 | 0.913 | 115.06 | 0.914 |
| 9 | 422 | 132.4 | 0.843 | 135.5 | 0.833 | 135.15 | 0.834 |
| 10 | 333,511 | 151.8 | 0.795 | 157.7 | 0.786 | 157.21 | 0.786 |

^a Calculated 2θ and d for pure Ag are also shown for reference. The lattice constant of the film A shown in the table is 4.120 ± 0.005 Å.

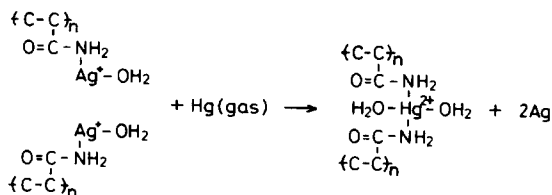


Fig. 7. Proposed reaction of PAAm-Ag⁺ complex with Hg gas.

ion chelates to two PAAm chains is indicated by gelation of PAAm solution observed upon adding Hg(NO₃)₂. This gelation may in turn affect the diffusion of Hg and Ag and, eventually, the progress of oxidation-reduction reaction itself.

In PAAm solution of high pH or without refining, there exist NH₃ molecules, which leads to the existence of [Ag(NH₃)₂]⁺ mentioned above besides the PAAm-Ag⁺ complex shown on the left side of Figure 7. Moreover, it is possible that some NH₃ molecules may take the place of coordinated H₂O. Then the rate of reaction shown in Figure 7 tends to be relatively reduced. Thus the progress of the oxidation-reduction reaction depends on NH₃ concentration.

The reason why Cu²⁺ ion does not produce an alloy is now clear: the oxidation-reduction reaction cannot take place, since the ionization tendency of Cu and the equilibrium constant to form PAAm-Cu²⁺ complex is high compared with that of Hg. Metals whose ionization tendency is lower than Hg, such as Pt and Au, have not been tried. The reason why other polymers such as PVA are not available for producing the film of interest is unknown. The different tendency in complex formation with Ag⁺ and Hg²⁺ in the other polymers from that in PAAm may be responsible.

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