

Contribution of Conformational Change of Polymer Structure to Electrochemomechanical Deformation Based on Polyaniline

KEIICHI KANETO* AND MASAMITSU KANEKO

*Department of Computer Science and Electronics,
Kyushu Institute of Technology, Iizuka, Fukuoka, 820-8502 Japan,
E-mail: kaneto@life.kyutech.ac.jp*

Abstract

The pH dependencies of electrochemomechanical deformation (ECMD) including the cyclic voltammetry and the expansion ratio in conducting polymers, polyaniline (PANI), and poly(*o*-methoxyaniline) film were studied to elucidate the mechanisms. It was found that the ECMD is governed by the conformational change of polymer structure as well as the insertion of bulky ions in the manner of comparable magnitude. Expansion ratios >20% in the ECMD were demonstrated for the thickness direction of PANI film. The results suggest that the magnitude of ECMD can be improved by choosing the preparation method of films.

Index Entries: Artificial muscles; electrochemomechanical deformation; conducting polymers; polyanilines; pH dependence.

Introduction

Recently, actuators (1) that generate flexible and soft movement such as bending, expansion, and twisting have generated much interest, because these exotic motions resemble natural muscles and are demanded for medical equipment, robotics, and replacement of human muscle in the future. Various kinds of flexible and soft actuators have been fabricated using polymers (2–4), gels (5), ion-exchange membrane, and nanotubes (6), which are driven in electrolyte solutions. There have been many studies on the electrochemomechanical deformation (ECMD) in conducting polymers such as polyaniline (PANI) (4), its derivatives (7), and polypyrrole (8,9), which are synthesized either chemically or electrochemically. ECMD has

*Author to whom all correspondence and reprint requests should be addressed.

been studied qualitatively by fabricating bimorph actuators (8) and quantitatively by the direct measurement of expansion and contraction of films (10) in electrolyte solutions. In our previous studies (7,10–12), the basic behaviors such as the typical expansion ratio and the contraction force were found to be about 3% along film and 2 to 3 MPa, respectively, in PANI films. On stepwise potential application to films, the response time of ECMD has been estimated to be 2 to 3 s (10,11).

The mechanisms of ECMD have been proposed (10–12): the insertion and dedoping of bulky ions, the conformational change owing to the delocalization of π -electron, and the electrostatic repulsion between polycations. However, there have not been any definitive studies to clarify these mechanisms. Simply, the first mechanism has been conjectured to be the primary mechanism (2,4,8). However, there have been ECMD behaviors of which the magnitude of ECMD did not depend on the kind of anion in poly(*o*-methoxyaniline) (PmAn) film at a certain pH (11). This fact has not been explained satisfactorily by the first mechanism alone. The latter two mechanisms should be involved and are desirable to fabricate artificial muscles exhibiting larger and quicker responses. Therefore, it is important to clarify the intrinsic mechanism of ECMD in conducting polymers.

In this article, the background of the electrochemistry of PANI, pH dependencies of ECMD in PANI, and PmAn films are discussed. The anisotropy of ECMD of films along the film surface and thickness directions are also discussed.

Background of Electrochemistry and ECMD Behaviors in PANI Films

PANIs undergo three typical redox stages (13), depending on the pH of aqueous electrolyte solution, as shown by the cyclic voltammogram curve and chemical structures in Fig. 1. The half redox potential, $E_{1/2}$, is defined by $E_{1/2} = (E_a + E_c)/2$, in which E_a and E_c are anodic and cathodic potentials at the peak currents for oxidation and reduction, respectively. The most electrically conductive state is the emeraldine salt (ES) that is between pernigraniline salt (PS) at the higher potential side and the leucoemeraldine salt (LS) at the lower potential side (13). Both LS and PS states are insulators.

In the oxidation process from LS to ES, two electrons are withdrawn, simultaneously two chloride ions are doped, or two protons are ejected per four benzene units, depending on the pH of the electrolyte solution, as discussed later. For the oxidation from ES to PS, two electrons are withdrawn and two protons are ejected from the film. The bottom of Fig. 1 shows the typical ECMD behavior of the PANI film along the stretched direction (14). The film at the LS expands by the oxidation or potential sweep to the higher side and shows the maximum length at the ES. Then the film contracts slightly above the ES state at higher potentials. When the potential is returned from the PS, the film expands slightly, then contracts

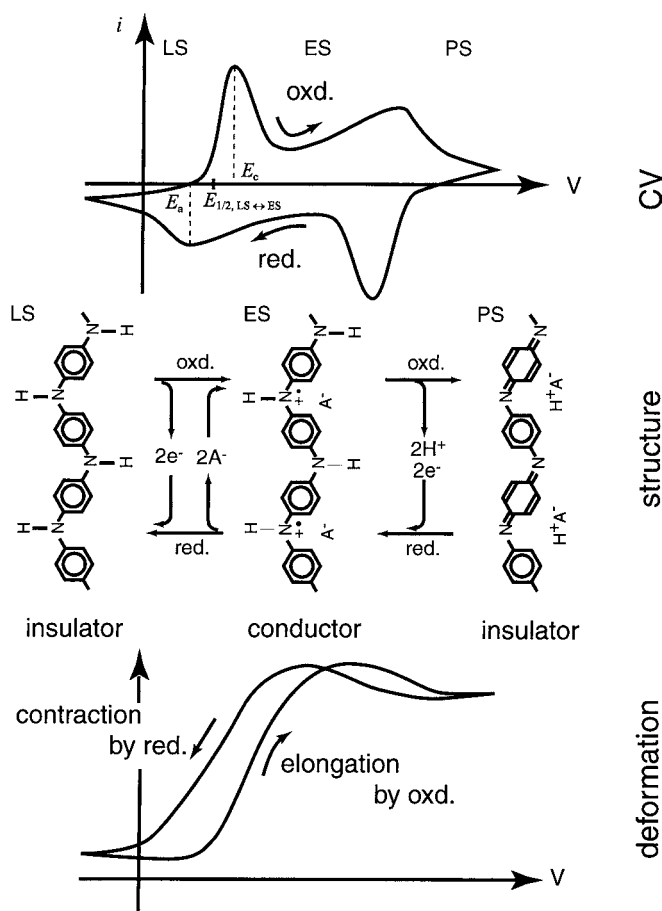


Fig. 1. **(Top)** Typical cyclic voltammogram (CV), **(middle)** redox behavior in chemical structures, and **(bottom)** expansion and contraction of PANI film along the stretched direction.

below the potential of $E_{1/2, LS \leftrightarrow ES}$, and returns to the original length. Interestingly, the basic behavior of ECMD is very similar to the result of weight change of PANI film monitored by the quartz crystal microbalance (15). Namely, the quartz crystal microbalance data show the maximum weight at ES, which suggests that the ECMD resulted from the insertion and ejection of bulky ions. However, when we take into consideration the fact that the ES is the most conductive state, the latter two proposed mechanisms of ECMD are not excluded as the origins of expansion.

Materials and Methods

Sample Preparation and Measurements of ECMD

PANI and PmAn were prepared by oxidative electrochemical polymerization of aniline and *o*-methoxyaniline by a method similar to one

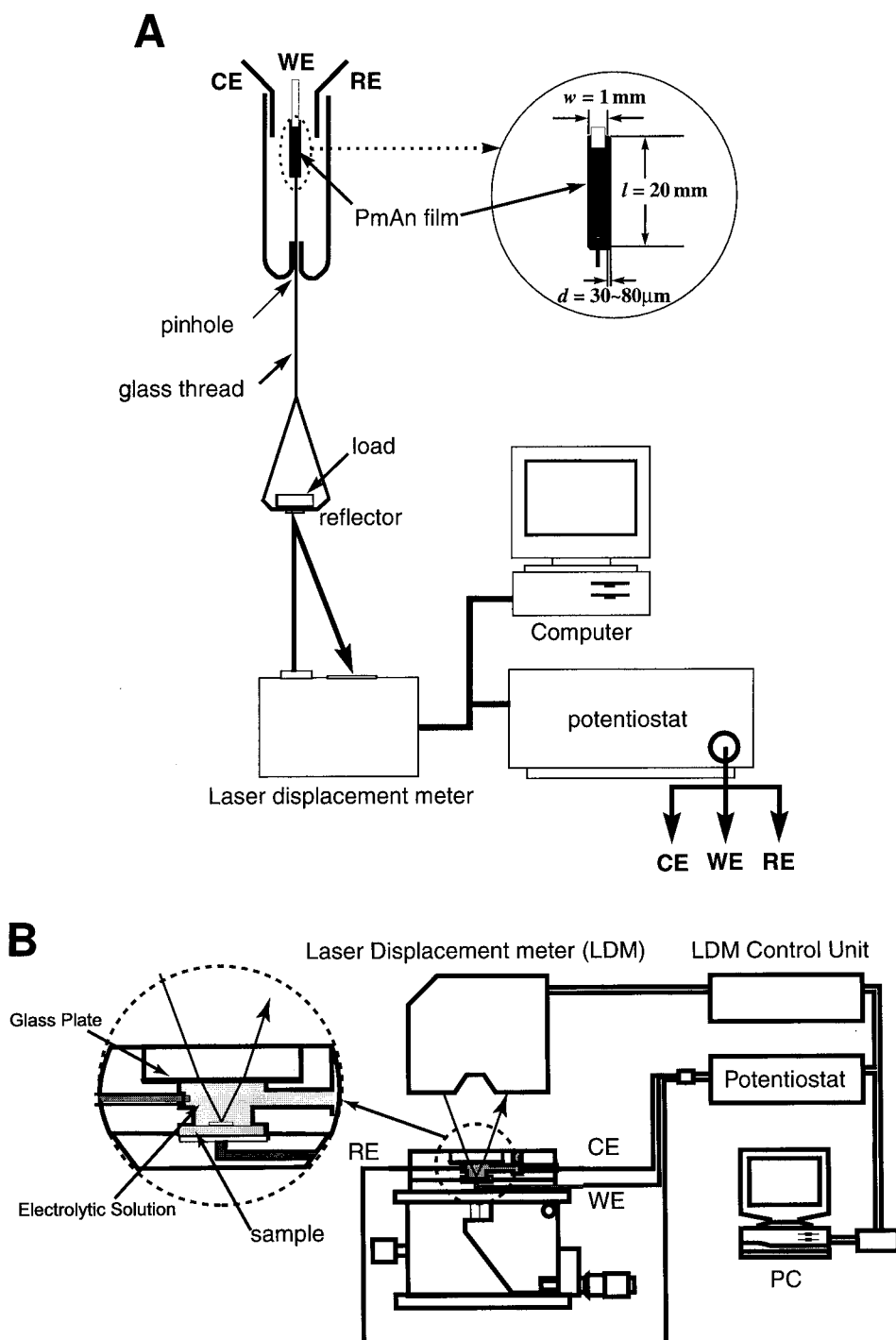


Fig. 2. Schematic diagrams for the measurement of electrolytic expansion along (A) the film length and (B) thickness direction. WE, CE, and RE are working electrode, counterelectrode, and reference electrode, respectively.

described in our previous studies (10,11,13). First, 0.1 M aniline and 1 M HCl aqueous solution were mixed with a solution of 0.3 M ammonium peroxydisulfate and 1 M HCl for 3 to 4 h at about 5°C. The obtained paste was then washed with 1 M HCl several times and deprotonated with 1 M NH_4OH . Next, the product, emeraldine base, was dried in vacuo and dissolved in *N*-methyl-2-pyrrolidone (NMP) at a concentration of 5 wt%. Finally, the emeraldine base films were prepared by casting the NMP solution on a glass plate. The cast film obtained by this method can be stretched mechanically more than three times the original length.

The ECMD along the film surface (14) and also the thickness direction (7) were examined to investigate the anisotropic behaviors. For the measurement of ECMD along the film surface, a special cell with a pinhole at the bottom, as shown in Fig. 2A, was employed. Change in film length was detected by a thread connected to the bottom end of the film through the pinhole. The ECMD for the thickness direction was measured by the cell shown in Fig. 2B. Change in the film dimensions was monitored with a laser displacement meter (Keyence LC-2430) with an accuracy of 10 nm. The cells were driven by a power supply of a potentio/galvanostat, and the redox current and the response of ECMD were measured and processed by a personal computer. The relationship between the degree of oxidation and the rate of expansion ($\Delta l/l_0$; l_0 is the original length) was estimated from the cyclic voltammogram and the change in film length (Δl) by the application of linear voltage sweep.

Results and Discussion

Dependencies of Expansion Ratio on Degree of Oxidation and Electrolytes

The dependencies of the $\Delta l/l_0$ on the level of reduction, y , for various kinds of electrolytes in PANI films (10) at pH 0.0 are shown in Fig. 3. In Fig. 3, y was determined from the amount of electrically injected electrons during the potential sweep in the cyclic voltammogram, and the definition is given at the bottom of the figure. That is, $y = 0$ is the basis of the ES state, and, thus, $y = -0.5$ and 0.5 are the LS and PS states, respectively. The expansion ratio of PANI films at pH 0.0 strongly depends on the kind of negative ions as seen in Fig. 3. The hysteresis of the curve originates from the nonequilibrium condition of the system owing to the slow rate of diffusion and also thermodynamics. Although the benzenesulfonic acid was extremely large, a small contraction was obtained. This finding could be explained by the fact that the benzenesulfonic acid was too large to penetrate into the film.

Figure 4 shows dependencies of the $\Delta l/l_0$ on the anion volume of electrolytes in PANI and PmAn films at pH 0.0. The contraction in the electrolyte of sulfuric acid is the smallest, since the sulfuric acid is a divalent anion. The $\Delta l/l_0$ of PANI depends on the electrolyte in the manner that the larger

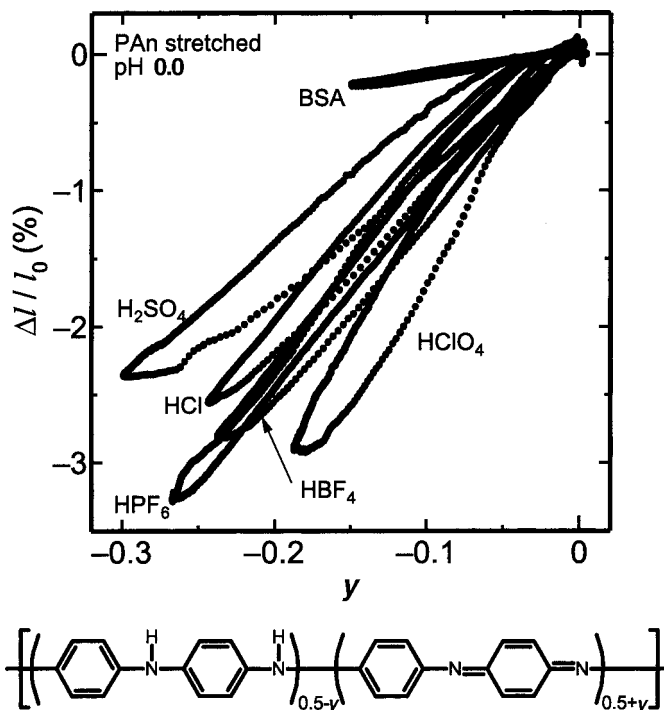


Fig. 3. Dependencies of the $\Delta l/l_0$ on the level of reduction, y , for various kinds of electrolytes in PANI (PAn) films at pH 0.0. The definition of y is shown at the bottom of the figure, and the ES state is taken as $y = 0$ as the basis of ES state, and l_0 is the length of film at $y = 0$. BSA, benzenesulfonic acid.

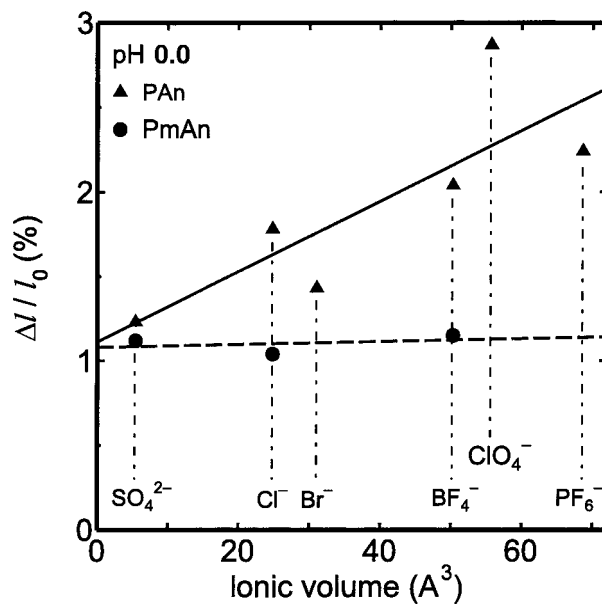


Fig. 4. Anion radius dependence of the $\Delta l/l_0$ in PANI (PAn) film and poly(*o*-methoxyaniline) at pH 0.0.

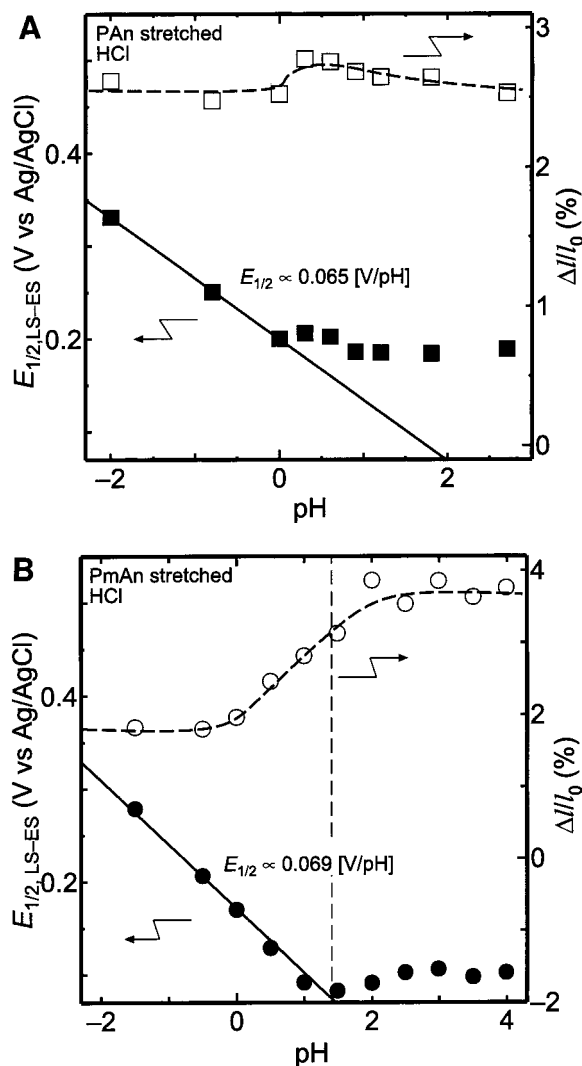


Fig. 5. pH dependencies of the $E_{1/2}$ and $\Delta l/l_0$ in (A) PANI (PAn) and (B) poly(o-methoxyaniline). The values of $\Delta l/l_0$ are taken at $y = -0.2$.

the ion, the more it expands (10). The result proves that the ECMD is surely owing to doping and dedoping of bulky ions for PANI. On the other hand, $\Delta l/l_0$ of PmAn is almost independent of the anions, indicating that the deformation of PmAn is operating by a different mechanism. Note that the expansion ratio at the extrapolation to the zero ion radius is a finite value of about 1% and not zero for both films. The finite value suggests that the latter two proposed mechanisms are taking place for the ECMD.

pH Dependence of ECMD

pH dependencies of the $E_{1/2}$ and $\Delta l/l_0$ in PANI and PmAn films (7) are shown in Fig. 5A and Fig. 5B, respectively. As evident from these results,

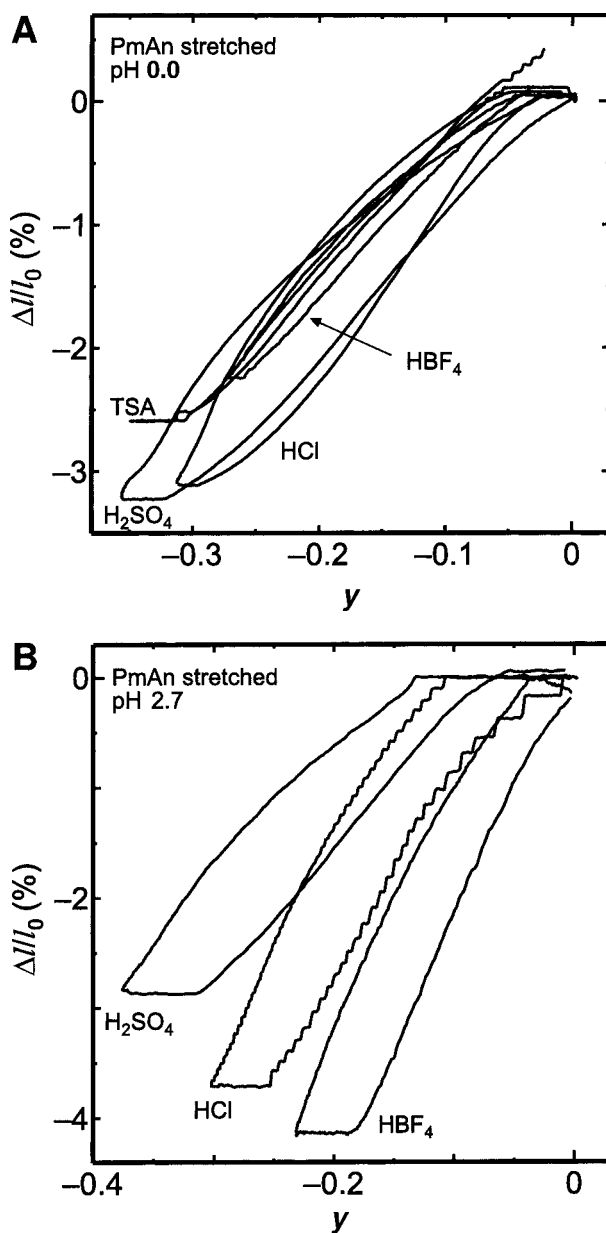


Fig. 6. Dependencies of $\Delta I/I_0$ in poly(*o*-methoxyaniline) films on various kind of acids at (A) pH 0.0, in which TSA is toluene sulfonic acid, and (B) pH 2.7.

the $E_{1/2}$ was pH dependent at pH < 0.0 and pH < 1.5 for PANI and PmAn, respectively. The gradients of the pH dependence were 60–70 mV/pH for both curves, indicating that a proton was ejected by the oxidation of an electron removal (13). That is, the expansion at pH < 0–1.5 resulted from the conformational change in polymer structure and the electrostatic repulsion. On the other hand, at pH > 0 and pH > 1.5 for PANI and PmAn,

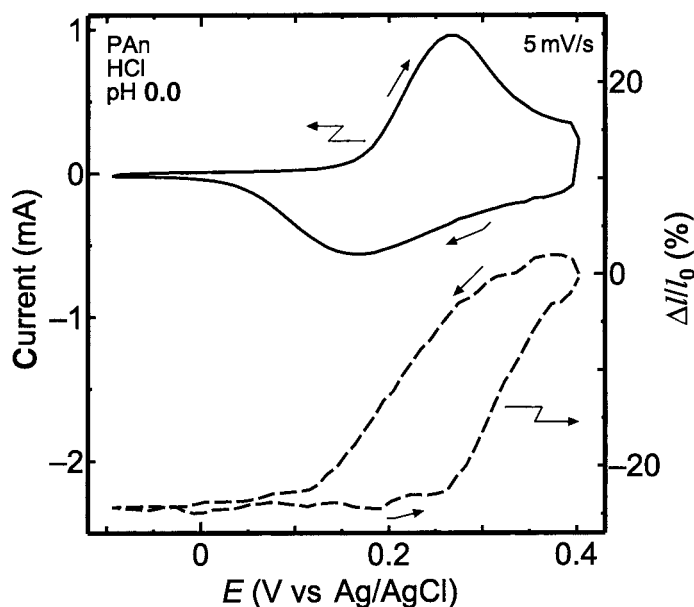


Fig. 7. Cyclic voltammogram curve and (bottom) $\Delta l/l_0$ for the thickness direction of a PANI (PAn) cast film.

respectively, the $E_{1/2}$ was independent of the pH, suggesting that anions were injected by the oxidation. The difference in the magnitudes of the expansion ratios at lower and higher pH values, which is clearly seen in PmAn film, can be definitively attributed to volumes of the inserted bulky anions plus protons.

The dependencies of ECMD behaviors in PmAn film on the kind of anions for pH 0.0 and 2.7 are shown in Fig. 6A and Fig. 6B, respectively. Interestingly, at pH 0.0 the expansion rate scarcely depended on the kind of anions (11), as shown Fig. 6A; however, at pH 2.7 a remarkable dependence was observed, as depicted in Fig. 6B. Note that at pH 0.0 even in the electrolyte with large anions of toluene sulfonic acid, the expansion ratio was similar to that of H_2SO_4 and others. This finding clearly indicates that at pH < 1.5 in PmAn, the ECMD is surely driven by the change in polymer conformation and/or the electrostatic repulsion. At pH > 1.5 the film expanded by the conformational change with the cooperation of the insertion of bulky anions.

Anisotropy of Electrolytic Expansion in PANI Films

The electrochemomechanical expansion for the thickness direction in PANI cast film (7) showed an extremely large expansion ratio of >20%, as shown in Fig. 7, which is comparable with that of natural muscles (16). A similar result was also obtained in the cast film of PmAn for the thickness direction (11). Figure 8 shows the anion dependence of expansion ratios for the thickness direction in PANI, indicating that an expansion ratio of >20% does not depend on the volume of anions. The large expansion ratio for the

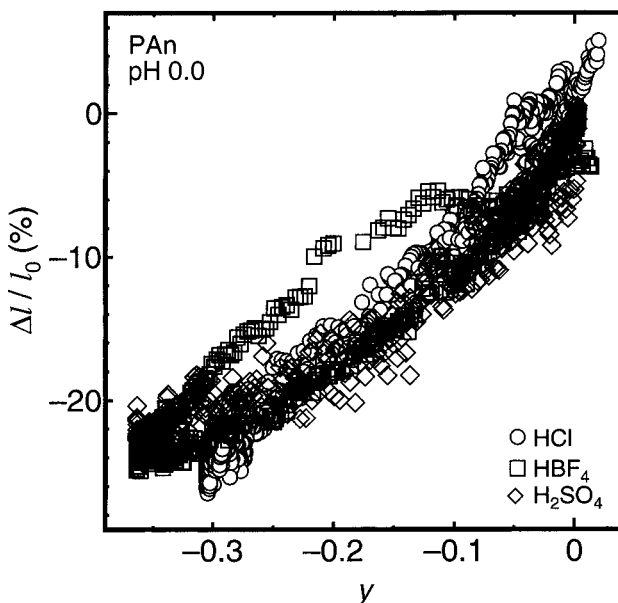


Fig. 8. Expansion ratio against degree of oxidation for the thickness direction in PANI (PAn).

thickness direction is conjectured to relate to the condensation process of the cast film. The evaporation of NMP solution results in shrinking only in the thickness direction, but not in the area. Therefore, the cast film has more freedom to expand to the thickness direction than that of parallel direction to the film surface.

Conclusion

It has been clarified that the changes of molecular conformations due to the delocalization of π -electron and also the electrostatic repulsion between the polycations are taking place as a mechanism of ECMD as well as the insertion of bulky anions in conducting polymers. By investigating the molecular structure and the higher-order structure to optimize the ECMD, it will be possible to improve the expansion ratio and the force for the practical actuators with better ability than that of natural muscles.

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