Physicochemical and Electrical Characterization of Polyaniline Induced by Crosslinking, Stretching, and Doping

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The polyaniline films with various insoluble parts are fabricated. The oxidation state (1-y) of these polyaniline is 0.53 and 0.54, respectively. To control the interchain and intrachain interaction of the polymer, the polyaniline films are stretched with appropriate ratio. The insoluble part of polyaniline synthesized at room temperature (low molecular weight) is 12%-76% and that of polyaniline synthesized at 0 °C (intermediate molecular weight) is 65%-89%. The low molecular weight polyaniline films with various drawing ratios have amorphous structure. In the intermediate weight polyaniline films, the crystallinity of films increases with drawing ratio as well as insoluble part. The difference of the insoluble part affects electrical conductivity which is increased dramatically with draw ratio. In particular, the higher insoluble part caused greater increase in electrical conductivity.

Introduction

The conducting polymer is unique type polymer, which has π-conjugated electrons spread along the polymer backbone and has delocalized electron structure after doping. Polyaniline is one of the most stable and popular conducting polymers.[1] Polyaniline can be classified as three kinds (leucoemeraldine base, emeraldine base, and pernigraniline base) by its oxidation state.[2,3] Since Angelopoulos *et al.*[4] have found NMP(*N*-methyl-2-pyrrolidinone) as a good solvent, for emeraldine base, many researchers make an effort to verify the intrinsic property of conducting polymers in processing. For instance, polyaniline film, fiber, elastomer and blend were produced from the NMP solution, and the crystallinity, orientation of polymer chain, morphology, and conduction characteristics of these materials were investigated.

The molecular weight and its distribution of polymer chains which can be controlled by synthetic condition affect the mechanical properties of polymer. According to the previous reports, the weight-average molecular weight (Mw) of polyaniline is about 70,000 when it was synthesized at 0 °C[5] and about 430,000 at -35 °C,[6] respectively. The polymer solution is prepared by dissolving polyaniline with various molecular weights in NMP and the films can be fabricated from polymer solutions. In the literature, when polyaniline films were stretched in equal ratio, the high molecular weight polyaniline film showed higher crystallinity and electric conductivity.[7]

MacDiarmid *et al.*[2] systematically investigated the change of electric conductivity of polyanilines by protonic acid doping. They presented the variation of electrical conductivity for emeraldine hydrochloride synthesized with chemical and electrochemical methods as a function of pH (concentration of HCl solution). The electrical conductivity of these polymers are about 1 S/cm at pH = -1– +1, and 10^{-10} S/cm at pH=5-6, respectively. Recently, it has been reported[7] that the electrical conductivity of polyaniline is largely affected by polymer chain alignment and the crystallinity formed by the alignment of polymer stretching. The electrical conductivity of polyaniline films which are stretched to fourfold increases from 5 S/cm to 170 S/cm after doping with 1 M HCl.

In the conducting polymer, the fields of study and practical applications were selected according to the electric conductivity of polymer. Therefore, in this research, polyaniline powder with low and intermediate molecular weight are manufactured and films which have different insoluble part were cast from the NMP solution of each sample. These films were stretched in appropriate ratio to transform their interchain or intrachain interaction. In order to find out the factors that affect electrical properties of polyaniline film, the changes of the crystallinity and electrical conductivity of polyaniline film were investigated. This investigation can contribute to developing polyaniline with higher electrical conductivity and processibility.

Experimental

The detailed synthetic procedure to prepare polyaniline was followed the method which is reported by MacDiarmid *et al.*.[8] We synthesized low molecular weight polyaniline (LMW-PANI) powder using more oxidant than stoichiometric amount at room temperature (30 °C). And the synthesis of intermediate molecular weight polyaniline (IMW-PANI) powder was proceeded at 0 °C. The rest of the steps are same.

We prepared several films with various insoluble parts by dissolving polyaniline powder in NMP, pouring it on the glass substrate (14 cm×14 cm×0.5 cm) slowly, and drying it in the oven at 75 °C. For changing the alignment of polymer chain in the film, the cast film was stretched to fourfold at 100-150 °C. The stretched films were soaked into HCl solution for 48 hours to accomplish the protonic acid doping.

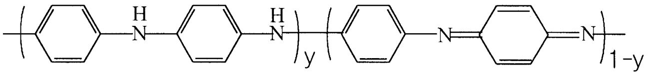
The oxidation state of polyaniline can be determined by relative concentrations of benzenoid ring and quinoid ring in the polymer chain. For obtaining the concentrations of two basic units, the polyaniline powder sample and excess amount of the Ti^{3+} solution ($TiCl_3$, the concentration is known) which converts quinoid ring into benzenoid ring in the polyaniline are mixed in acetic acid solvent. The reaction which is reducing qunoid ring to benzenoid ring is occurred. After the reaction, the extra Ti^{3+} solution can be back-titrated with Fe^{3+} solution ($FeNH_4(SO_4)_2 \cdot 12H_2O$, the concentration is known). In here, Fe^{3+} which is changed to Fe^{2+} converts Ti^{3+} into Ti^{4+}). When Ti^{3+} are all consumed in this titration, the extra Fe^{3+} does not react further but displays color by indicator (5% NaSCN). From this, we could find the amount of Ti^{3+} solution consumed in the reaction. Then, we calculate the amount of quinoid ring and verify the oxidation state of synthesized polyaniline.

In order to analyze the insoluble part of the films from solution casting methods, reference sample and measuring sample are prepared. We measured the initial weight of the sample which is corrected by solvent content of reference sample. The insoluble part of the film was determined as follows; i) The measuring sample film put into NMP. ii) The soluble part of film is dissolved slowly in NMP. iii) The dissolution of the film is proceeded until the color of NMP is not changed. If some soluble part of the film remained, the color of solution is blue. iv) After dissolution of film, the sample film was taken out from NMP and rinsed with CH_3OH. v) After the film was vacuum dried for 12 hours, we measured the final mass of the sample which is corrected by solvent content of this film. The solvent content of films are determined by TGA at room temperature ~300 °C with scan rate 5 °C/min in N_2 atmosphere. Finally, we can calculate the insoluble part from the ratio of initial and final mass of sample.

To examine the degree of alignment and crystallizing of polymer chains, we used Philips PW 1825/00 X-ray diffractometer with Ni-filtered Cu Kα radiation (λ=1.5418 Å) by 0.05°/sec scan in $5^\circ \leq 2\theta \leq 35^\circ$. The electrical conductivity was examined by four-probe method. The potential and current were measured independently in order to remove the contact resistance between platinum electrode and sample.

Results and Discussion

Polyaniline can be classified as follow by its oxidation state.



Where 1-y=0.0 is leucoemeraldine base, 1-y=0.5 is emeraldine base, and 1-y=1.0 is pernigraniline base. The analysis of oxidation state (1-y) for polyaniline, which was calculated by the amount of quinoid ring, showed that oxidation state of low molecular weight polyaniline is 0.53 and that of intermediate molecular weight is 0.54. In general, the polyaniline synthesized at N_2 atmosphere has oxidation state around 0.4 and that synthesized at air has almost 0.6. Here, the reason for 1-y having bigger value than 0.5 would be the fact that it was made in air.

To calculate the insoluble part for the films which were casted with NMP solutions of various weight percentage, this equation is used.

$$\text{Percentage of insoluble part (\%)} = \frac{(W_{\text{final}} - W(\text{samp.})_{\text{solution}})}{(W_{\text{initial}} - W(\text{ref.})_{\text{solution}})} \times 100$$

Where W_{initial} is initial weight of the sample film and W_{final} is final mass of the sample film after dissolving the soluble part. $W(\text{ref.})_{\text{solution}}$ is the solvent content of reference films which are determined by TGA and $W(\text{samp.})_{\text{solution}}$ is the solvent content of sample films after dissolving the soluble part. The results of this analysis are shown in Table 1. From this result, the insoluble part increases with weight percentage(wt%) of emeraldine base dissolved in NMP solution. If the weight percentage of film is same, low molecular weight polyaniline has lower percentage of insoluble part than the intermediate molecular weight one. The low molecular weight polyaniline has less opportunity to form insoluble part between the chains because it has the short polymer chain.

We investigated the correlation for the insoluble part, crystallinity, and molecular weight using X-ray diffraction analysis. Figure 1-(a) and (b) show the X-ray diffraction patterns of the films which are prepared with low and intermediate molecular weight polyaniline with different percentage of insoluble part. Both low and intermediate molecular weight polyaniline have amorphous structure. Only the area of broad peak differs from each other. Figure 2-(a) shows X-ray diffraction patterns of the low molecular weight polyaniline film prepared by using 11 wt% EB-NMP solution with various drawing ratio. Although the draw ratio of the polyaniline films gets larger, the amorphous structure of the film maintained, but the area of the peaks is changed. Figure 2-(b) and (c) show the X-ray diffraction patterns of the intermediate molecular weight polyaniline films prepared with 3 wt% and 11 wt% EB-NMP solution. In these films, the crystallinity increases with the draw ratio. As mentioned above, all the low molecular weight polyaniline films have amorphous structure in spite of increasing the draw ratio of films. However, the intermediate molecular weight polyaniline films show large increase of crystallinity as the draw ratio gets larger with increasing percentage of insoluble part. In addi-

Table 1. The percentage of insoluble part of various polyaniline films with different molecular weight

Sample	Low molecular weight			Intermediate molecular weight		
EB/NMP(wt%)[a]	3wt%	5wt%	11wt%	3wt%	5wt%	11wt%
Percentage of insoluble part(%)	12.59[b]	55.29	76.34	65.38	80.30	88.91

[a] EB is emealdine base and NMP is *N*-methyl-2-pyrrolidinone. [b] ±5% deviation.

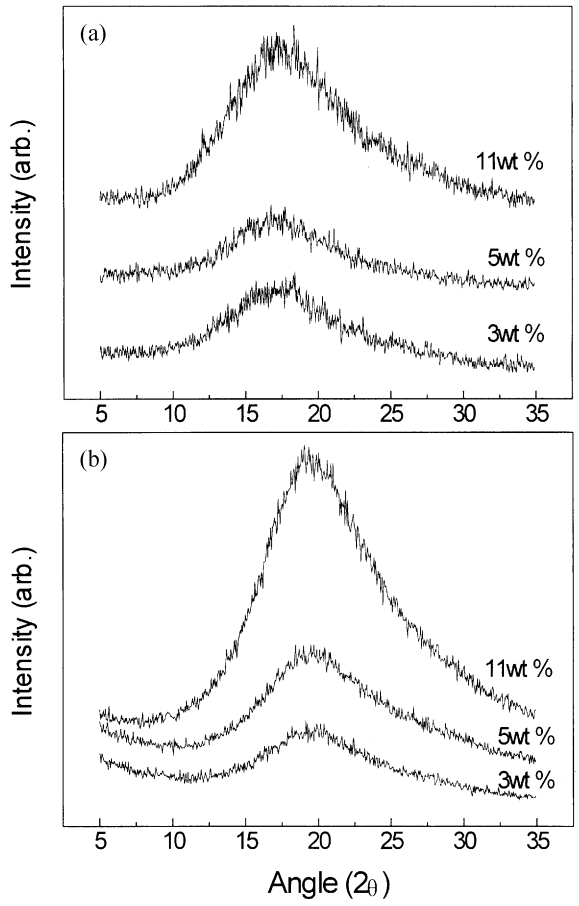


Figure 1. X-ray diffraction patterns of polyaniline films prepared from various weight percentage of NMP solution. (a) low molecular weight, (b) intermediate molecular weight.

tion, we find that the films with large insoluble part also have large increasing effect of crystallinity. From these results, the low molecular weight polyaniline film is expected to have little change of physical properties during the stretching of film.

In general, stretching of polymer film orients the polymer chain in drawing direction. This means the change of its array from three-dimensional structure (coil-like structure) to one-dimensional structure (rod-like structure). The one-dimensional array of polymer chain by stretching has more regulation in its structure. This regulation causes microcrystalline domains[9)], which makes partial crystallinity in X-ray diffraction pattern. If the insoluble part can be controlled, the film has better crystallinity with increasing the draw ratio. However, the low molecular weight film maintains amorphous pattern. This implies that the degree of crystallinity is related to the insoluble part and its molecular weight. In intermediate molecular weight polyaniline with long polymer chain, the insoluble part acts as a nuclear formation site which increases the crystallinity of the film through stretching. However, in low molecular weight polyaniline with short polymer chain, the connection between the chains is not effective to maintain the amorphous pattern.

To investigate the relation of the insoluble part and the electrical properties of films with various draw ratios, we

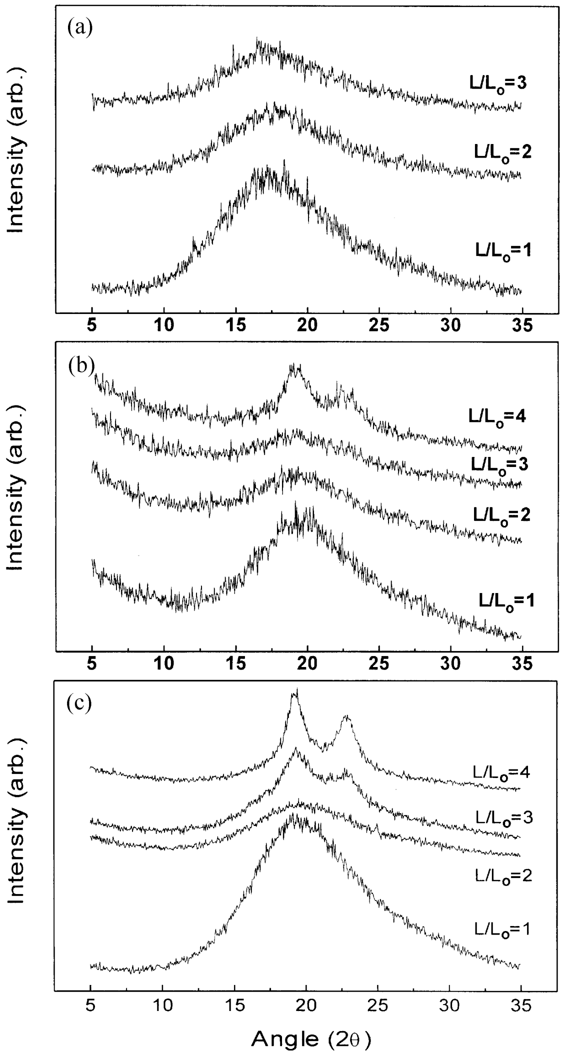


Figure 2. X-ray diffraction patterns of polyaniline films with various draw ratios. Films were cast from (a) 11 wt% low molecular weight, (b) 3 wt% and (c) 11 wt% intermediate molecular weight polyaniline in NMP.

Table 2. The electrical conductivity of polyaniline films with several draw ratios

Sample	EB/NMP wt %	L/L_o	σ (S/cm) at 298K
Low Molecular Weight	3 wt%[a]	1	16.5
	5 wt%	1 2 3	16.8 20.2 31.8
	11 wt%	1 2 3	17.8 30.5 33.4
Intermediate Molecular Weight	3 wt%	1 2 3 4	17.1 40.2 73.9 114.6
	5 wt%	1 2 3 4	17.7 42.1 94.4 123.4
	11 wt%	1 2 3 4	19.5 44.6 105.1 150.9

[a] The low molecular weight 3 wt% film is not elongated.

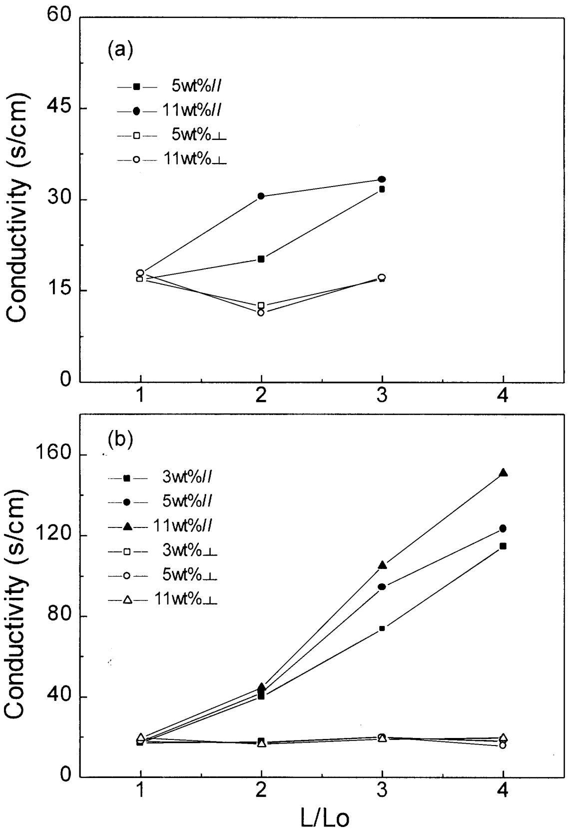


Figure 3. The relationship among the anisotropy of electrical conductivity, weight percentage, and draw ratio in the films. (a) low molecular weight, (b) intermediate molecular weight.

measured D.C. electrical conductivity. Table 2 shows the electrical conductivity at room temperature for low molecular weight and intermediate molecular weight polyaniline films doped with 1 M HCl, which have different percentage of insoluble part. When the film is not stretched, the electrical conductivity is slightly increased as the insoluble part increases. In case of stretching the film, the electrical conductivity increases drastically with the draw ratio and insoluble part. Therefore, the insoluble part itself does not affect the electrical conductivity of unstretched film, but it plays an important role when the film is stretched to orient the polymer chain. In addition, the increase of electrical conductivity implies that the changes in the polymer chain structure can vary the electrical properties through the transform processing.

The X-ray diffraction analysis and conductivity measurement indicate that the stretching of polymer film causes to orient the polymer chain in draw direction, which enlarges the regulation of structure and makes partial crystallinity in the polymer film. However, the film which has the low percentage of insoluble part or which was prepared from low molecular weight polyaniline maintains the amorphous structure notwithstanding the small electrical conductivity change. From these results, the site where the insoluble part is formed in polymer acts as the nuclear formation site. It increases the crystallinity upon stretching, and the polymer arranges as interlocking knuckle in small crystallinity domain. Thus the electrons as charge carriers, can be hopping between them.

In order to investigate the correlation among the anisotropy of electrical conductivity, the insoluble part in the film, and the film draw ratio, we measured the room temperature electrical conductivity of polyaniline film in parallel direction ($\sigma_{\parallel}$) (direction in which the film was stretched) and perpendicular direction ($\sigma_{\perp}$) (direction perpendicular to the one in which the film was stretched). The results are shown in Figure 3-(a) and (b). While $\sigma_{\perp}$ increases little, $\sigma_{\parallel}$ increases dramatically as the draw ratio increases. The measurement of the electrical conductivity in this direction gives great electrical conductivity value due to the improvement of mobility of charge carrier in the intrachain. Meanwhile, the measurement of electrical conductivity in perpendicular direction gives almost same value as initial state although the distance of interchain is closed. Because the charge carrier mobility of parallel direction in the polymer chains is main factor in increase of electric conductivity. In addition, intermediate molecular weight polyaniline film was found to have larger conductivity ratio ($\sigma_{\parallel}/\sigma_{\perp}$) than the low molecular weight one.

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