

# Preparation of Conductive Nylon 6 Film

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## Synopsis

Electrically conducting nylon 6 film was prepared by introducing amide group or cyan group into the nylon 6 film and then introducing  $\text{Cu}_x\text{S}$ , which is known as the *p*-type semiconductor, into the grafted nylon films. The graft copolymerization of acrylamide (AM) and acrylonitrile (AN) onto nylon 6 film was investigated using ceric salt as the initiator. The graft yield was influenced by the concentration of ceric salt, sulfuric acid and monomer, and the reaction time. The optimum conditions for the introducing of  $\text{Cu}_x\text{S}$  were studied. Electrical conductivity of  $\text{Cu}_x\text{S}$ -treated nylon film was found to be higher by order of  $10^9$  than that of the original nylon 6 film, and then properties of the resulting modified films were investigated.

## INTRODUCTION

During the last decade, much interest has been focused on improvement of the electroconductivity of polymers. Recently, it was reported in some patents<sup>1-3</sup> that if a certain metal complex in polyacrylonitrile was formed by a chemical modification on polymeric semiconductor with conductivity of  $10^{-1} \Omega^{-1} \text{cm}^{-1}$  could be obtained. This might suggest a new method for making an electrically conductive polymer from common polymers.

In previous reports,<sup>4-6</sup> it was shown that an electroconductive polyethyleneterephthalate (PET) film was obtained by grafting acrylamide (AM) and acrylonitrile (AN) on the film and then by introducing  $\text{Cu}_x\text{S}$ , a positive-type semiconductor. The resistivities of the  $\text{Cu}_x\text{S}$ -AM-*g*-PET and  $\text{Cu}_x\text{S}$ -AN-*g*-PET were 1780  $\Omega \text{cm}$  and 600  $\Omega \text{cm}$ , respectively, which is lower by order of  $10^{11}$  than that of the original PET film. Therefore, these  $\text{Cu}_x\text{S}$ -treated PET films could be regarded as a semiconductor.<sup>7</sup>

The present work was undertaken to improve the electrical conductivity of a nylon 6 film by grafting AM and AN on the film and then introducing  $\text{Cu}_x\text{S}$  onto the grafted film. Properties of the grafted and  $\text{Cu}_x\text{S}$ -treated nylon 6 film were also examined.

## EXPERIMENTAL

### Material and Reagents

Nylon 6 chips (Kolon Inc. RV = 2.6-2.8) were dried for 2 h at 105°C in a vacuum oven and a film with thickness of 0.3 mm was made of the dried nylon 6 chips using a heat press. The film Soxhlet extracted with petroleum ether for 8 h and dried in vacuum. It was kept in a desiccator before using. AM was purified by recrystallization in methanol, and AN was purified by common method.<sup>8</sup>

Ceric ammonium sulfate (CAS, Kokusan Chemical Works), cupric sulfate (Shinyo Pure Chemical Co., Ltd.), hydroxylamine sulfate (Junsei Chemical Co., Ltd.), and sodium thiosulfate (Hayashi Pure Chemical Co., Ltd.) were used without further purification.

### Graft Copolymerization

Graft copolymerization was carried out in a vessel in nitrogen atmosphere. The film samples were purified by swelling in 60% formic acid for 0.5 h, and neutralized with dilute ammonia water and then washed with water and dried in vacuum before grafting. These pretreated films were immersed in a solution of  $\text{H}_2\text{SO}_4$  and ceric ammonium salt (CAS) at  $60^\circ\text{C}$ . The temperature was maintained at  $60^\circ\text{C}$ , and the monomer was added to the reaction mixture.

After graft copolymerization, the nylon films were washed thoroughly to remove homopolymer. The homopolymer of AM in the graft was removed in boiling water, while the homopolymer of AN in the other graft Soxhlet extracted with DMF for 8 h. Both films were dried in vacuum and then weighed. The percentage of the graft yield was calculated as follows:

$$\text{Graft yield} = \frac{W_g - W_0}{W_0}$$

$W_0$  is the weight of the original sample before grafting, and  $W_g$  is the weight after grafting.

### Introducing of $\text{Cu}_x\text{S}$

Introduction of  $\text{Cu}_x\text{S}$  was carried out according to our previous papers.<sup>4,5</sup> AM-*g*-nylon or AN-*g*-nylon was immersed in a bath with an aqueous solution comprising cupric sulfate ( $\text{CuSO}_4$ ) and hydroxylamine sulfate [ $(\text{NH}_3\text{OH})_2\text{SO}_4$ ] and heated from room temperature to  $90^\circ\text{C}$  for adsorption of the monovalent copper ions sufficiently on it. Then sodium thiosulfate was added to the bath. After heat treatment, the films were rinsed well in cold water and dried completely. Effects of pH of the aqueous solution, concentration of each reaction reagents, reduction time, and reaction time on the introducing of  $\text{Cu}_x\text{S}$  were studied.

### Polymer Characterization

To identify the grafting of AM or AN to the nylon film, FT-IR spectra were investigated with a Nicolet DX System FT-IR Spectrometer by using the attenuated total reflectance (ATR) method.

To identify the introducing of  $\text{Cu}_x\text{S}$  onto nylon film, the X-ray diffraction intensity profiles of  $\text{Cu}_x\text{S}$  powder,  $\text{Cu}_x\text{S}$ -AM-*g*-nylon and  $\text{Cu}_x\text{S}$ -AN-*g*-nylon were examined with Ni-filtered  $\text{CuK}_\alpha$  radiation ( $35 \text{ kV} \times 20 \text{ mV}$ ) (Rigaku D/Max, Japan).

### Measurement of $T_g$ and $T_m$

$T_g$  and  $T_m$  of the samples are determined with differential scanning calorimeter (DSC) (Daini Seikosha SSC/560, Japan) in nitrogen atmosphere at a heating rate of  $5^\circ\text{C}/\text{min}$ .

### Measurement of Film Resistance

Surface resistance of the  $\text{Cu}_x\text{S}$ -treated samples was measured using Isolation Multimeter with two probes separated by 14 mm.

### Measurement of Conductivity

The conductivity of the samples was measured by four probe method with Electrometer (Keithley 616) and Potentiometer (Keithley 642).

The distance of each probe, which was made from platinum, was 2 mm. If the distance of each probe was equal, the conductivity was calculated by following equation:

$$\sigma = \frac{1}{2\pi S} \times \frac{I}{V}$$

Where  $\sigma$  is conductivity (S/cm),  $S$  is the distance of each probe, and  $I$  and  $V$  are current and voltage, respectively.

## RESULTS AND DISCUSSION

### Effects of Reaction Conditions on Graft Yield

It has been reported<sup>9-14</sup> that graft copolymerization with a ceric salt as an initiator is affected by the concentration of initiator, monomer, or acid, and time, and temperature of the reaction.

Figure 1 shows the effect of ceric ammonium sulfate (CAS) concentration on the graft yield. The percentage of grafting increases with an increase of CAS

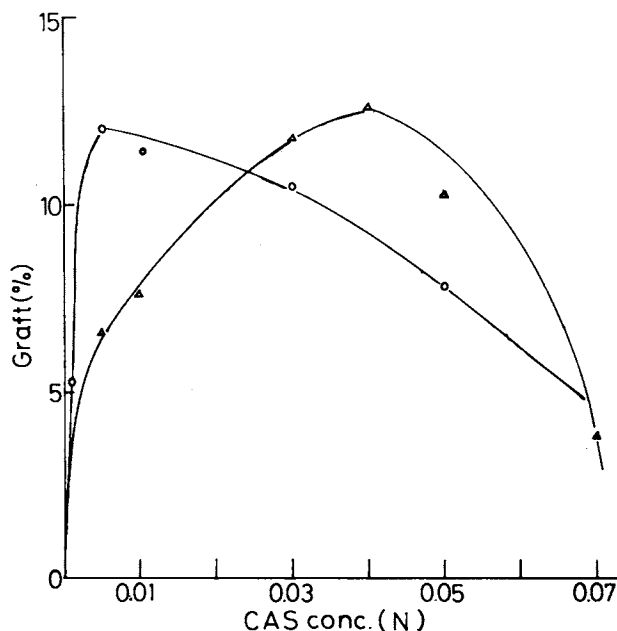


Fig. 1. Effect of CAS conc. on grafting of AM (○) and AN (△): swelling time, 30 min; reaction time, 2 h; temp, 60°C; acid conc. AM 0.1N and AN 0.5N; M:L = 1:100; monomer conc., 10%.

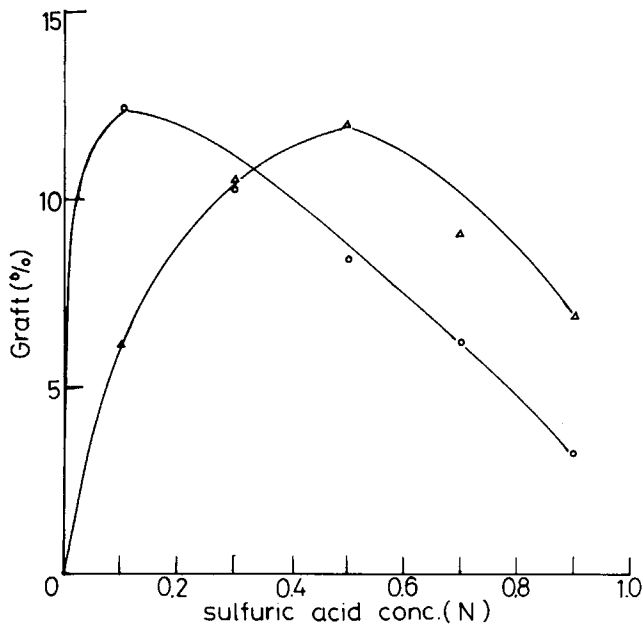


Fig. 2. Effect of sulfuric acid conc. on grafting of AM (○) and AN (Δ): swelling time, 30 min; monomer conc., 10%; temp, 60°C; reaction time, 2 h; M : L = 1 : 100; CAS conc., AM 0.005*N* and AN 0.04*N*.

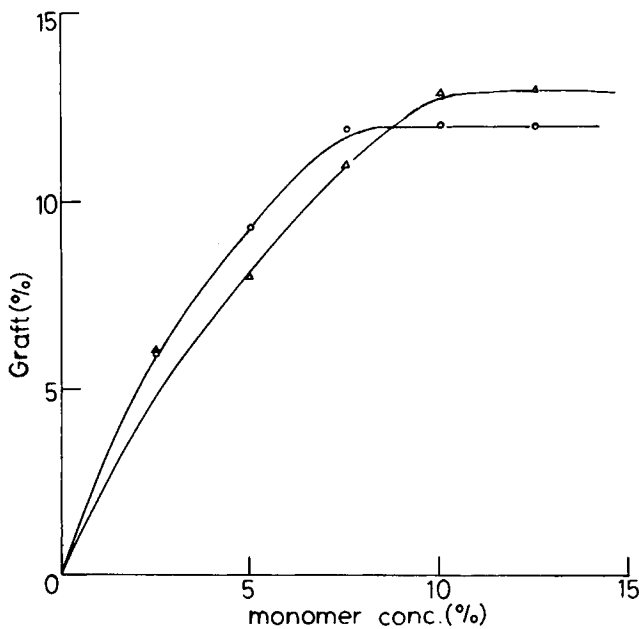


Fig. 3. Effect of AM (○) and AN (Δ) on grafting of nylon 6 film: swelling time, 30 min; reaction time, 2 h; temp, 60°C; CAS conc., AM 0.005*N* and AN 0.04*N*; M : L = 1 : 100; sulfuric acid conc., AM 0.1*N* and AN 0.5*N*.

concentration up to  $0.005N$  in the case of AM and up to  $0.04N$  in the case of AN. And then the yield falls upon further increase in CAS concentration obviously due to the predominance of termination of growing graft chains  $Ce^{4+}$ .

Figure 2 shows the effect of acid concentration on grafting. There was an increase in AN grafting yield up to  $0.5N$   $H_2SO_4$  and AM graft yield up to  $0.1N$   $H_2SO_4$  followed by a decrease in the yield with the higher concentration.

This leads to the conclusion that the increase in  $H^+$  concentration should suppress the generation of radicals. This means that, with the increase in  $H^+$  concentration, the graft yield should be reduced. Depending on the reactivity of monomers, this value will change, and hence we get different values of optimum  $H_2SO_4$  concentration in both cases. The effect of monomer concentration on the graft yield is shown in Figure 3

It can be seen that, as the monomer concentration was increased to 7.5% in AM grafting and to 10% in AN grafting, the graft yield also increased. Further increases in monomer concentration do not enhance the graft yield. This suggests that there is an optimal concentration of monomer for the maximum grafting. Beyond this concentration, much of the monomer seems to be physically absorbed on the nylon films and impedes diffusion of the initiator inside the films; thereby the graft yield is constant. The effect of time on graft copolymerization is illustrated in Figure 4. As expected, it is shown that the graft yield increases with an increase of reaction time up to 1 and 2 h in the case of AN and AM, respectively, and then levels off after about 4 h.

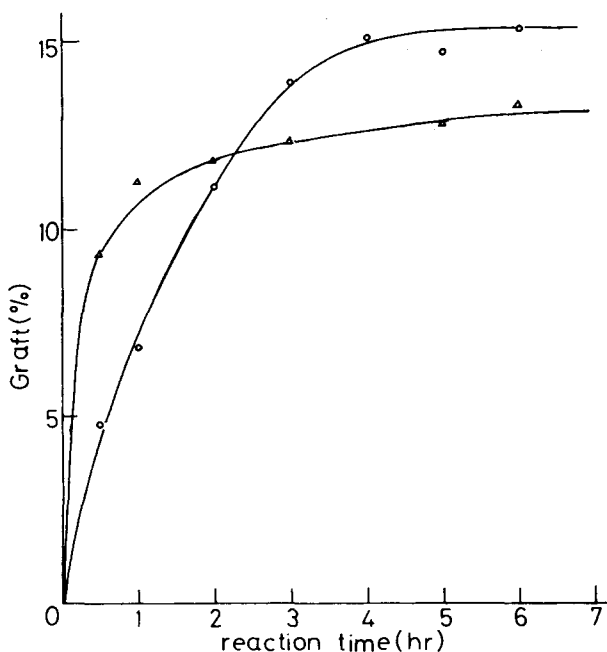


Fig. 4. Effect of reaction time on grafting of AM (○) and AN (△): swelling time, 30 min; monomer conc, 10%; temp,  $60^{\circ}C$ ; CAS conc, AM  $0.005N$  and AN  $0.04N$ ; M : L = 1 : 100; reaction time, 2 h; sulfuric acid, AM  $0.1N$  and AN  $0.5N$ .

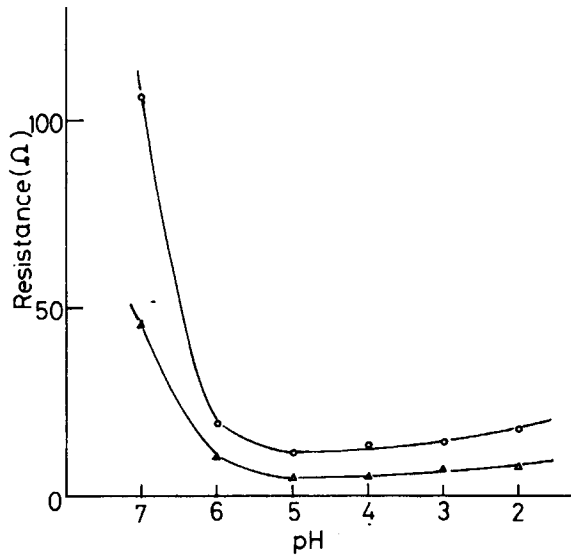


Fig. 5. Average surface resistance at different pH: (○)  $\text{Cu}_x\text{S-AM-g-nylon}$ ; (△)  $\text{Cu}_x\text{S-AN-g-nylon}$ ; reduction time, 2 h; reaction time, 4 h; cupric sulfate, 48 g/L; hydroxylamine sulfate, 32 g/L.

#### Effect of Reaction Conditions on the introducing of $\text{Cu}_x\text{S}$

The effect of pH of the aqueous solution on the introducing of  $\text{Cu}_x\text{S}$  onto nylon 6 film was studied as shown in Figure 5, since it has been reported<sup>15,16</sup> that the pH plays an important role in the absorption of cuprous ion. The resistance falls fast with decrease of the pH up to pH 6 and changes little with the further decrease.

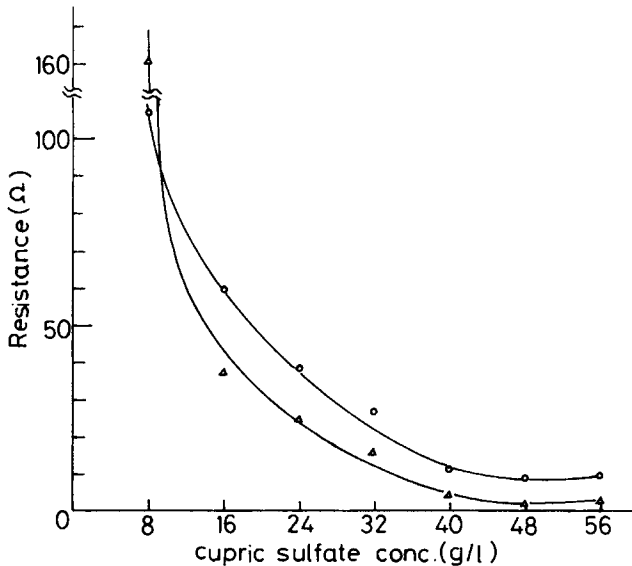


Fig. 6. Average surface resistance at different cupric sulfate conc: (○)  $\text{Cu}_x\text{S-AM-g-nylon}$ ; (△)  $\text{Cu}_x\text{S-AN-g-nylon}$ ; reduction time, 2 h; reaction time, 4 h; hydroxylamine sulfate, 32 g/L; sodium thiosulfate, 48 g/L.

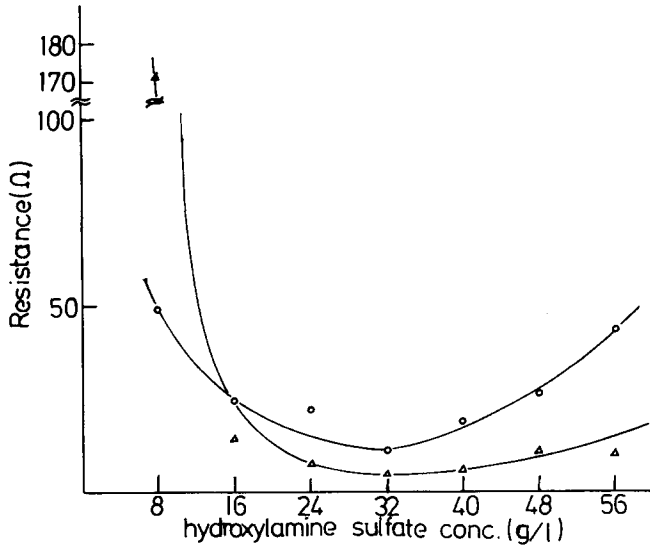


Fig. 7. Average surface resistance at different hydroxylamine sulfate conc: (○) Cu<sub>x</sub>S-AM-g-nylon; (Δ) Cu<sub>x</sub>S-AN-g-nylon; reduction time, 2 h; reaction time, 4 h; cupric sulfate, 48 g/L; sodium thiosulfate, 48 g/L.

The CuSO<sub>4</sub> concentration dependence of the surface resistance is shown in Figure 6. The resistance of the films decreased steadily with an increase of CuSO<sub>4</sub> concentration up to 48 g/L, and further decrease was not founded.

The effect of concentration of hydroxylamine sulfate as a reducing agent on the resistance is shown in Figure 7. It can be seen that the resistance of films

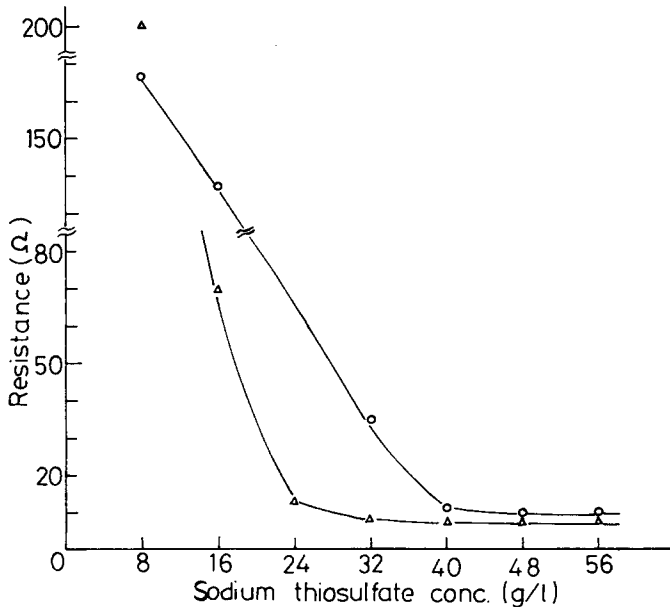


Fig. 8. Average surface resistance at different sodium thiosulfate conc: (○) Cu<sub>x</sub>S-AM-g-nylon; (Δ) Cu<sub>x</sub>S-AN-g-nylon; reduction time, 2 h; reaction time, 4 h; cupric sulfate, 48 g/L; hydroxylamine sulfate, 32 g/L.

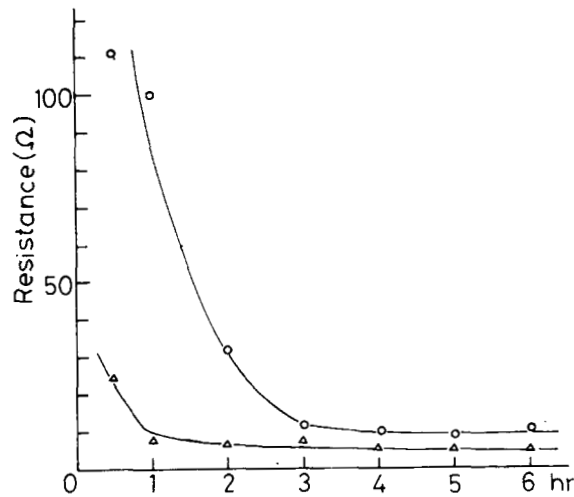


Fig. 9. The variation of average surface resistance in reduction time: (○)  $\text{Cu}_x\text{S-AM-g-nylon}$ ; (Δ)  $\text{Cu}_x\text{S-AN-g-nylon}$ ; reaction time, 4 h; cupric sulfate, 48 g/L; hydroxylamine sulfate, 32 g/L; sodium thiosulfate, 48 g/L.

decreased with increasing hydroxylamine sulfate concentration up to 32 g/L and then increased upon further increase in hydroxylamine sulfate concentration. This means that, beyond this concentration, hydroxylamine sulfate cannot act as a reducing agent any more.

Figure 8 shows the sodium thiosulfate concentration dependence of resistance. The resistance of films was almost independent of the sodium thiosul-

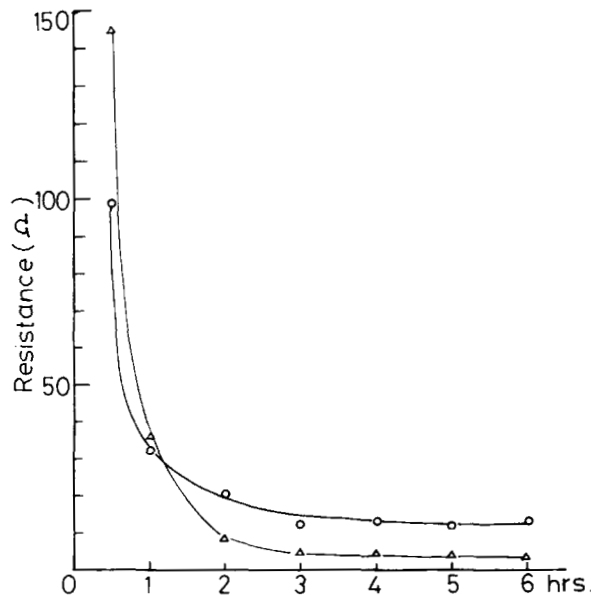


Fig. 10. The variation of average surface resistance in sodium thiosulfate reaction time: (○)  $\text{Cu}_x\text{S-AM-g-nylon}$ ; (Δ)  $\text{Cu}_x\text{S-AN-g-nylon}$ ; reduction time, 2 h; cupric sulfate, 48 g/L; hydroxylamine sulfate, 32 g/L; sodium thiosulfate, 48 g/L.



fate concentration at concentration more than 40 g/L while that of films decreased with an increase of concentration at less than 40 g/L.

This leads to the conclusion that the amounts of the copper compound, the reducing agent, and the sulfur compound should influence the amount of absorbed copper sulfide.

Figures 9 and 10 show the effect of reduction time and reaction time on the resistance, respectively. The resistance of the films decreased with an increase of reduction and reaction time up to 3 h and leveled off after about 3 h. Beyond this reaction time, the films are saturated with  $\text{Cu}_x\text{S}$  and diffusion of  $\text{Cu}_x\text{S}$  into the nylon films is impeded.

### Characterization

Figure 11 shows the FT-IR spectra of original nylon, AM-g-nylon and AN-g-nylon films. In the case of AM-g-nylon, the  $-\text{CH}_2-$  band of vinyl group

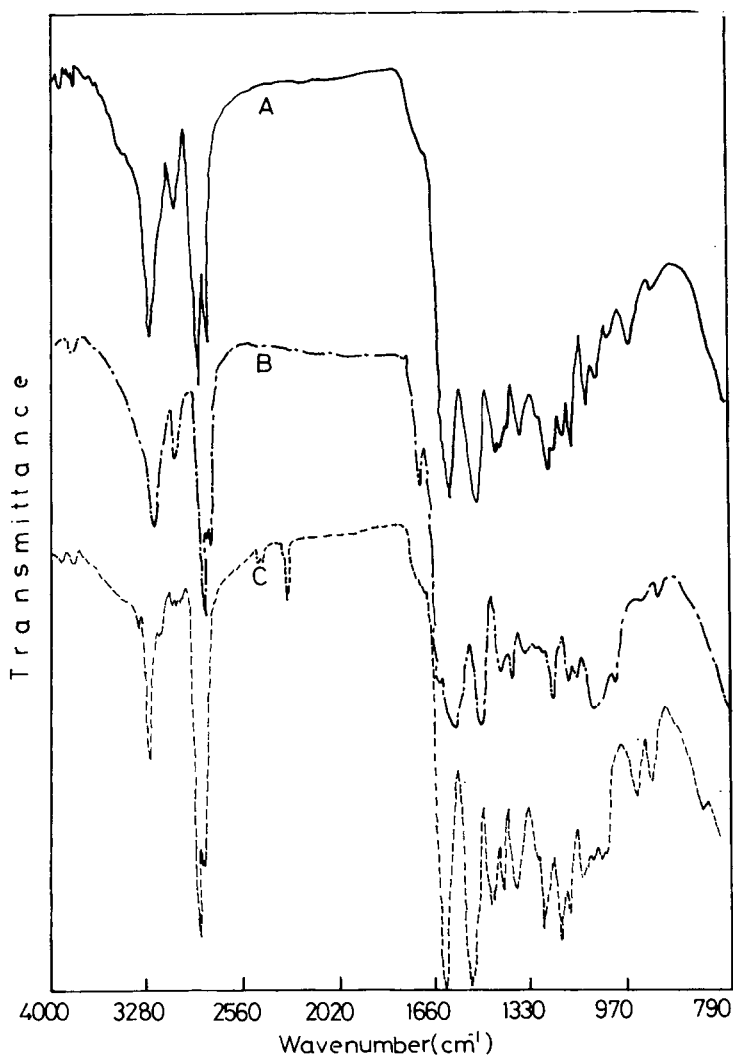


Fig. 11. FTIR spectra of nylon (A), AM-g-nylon (B), and AN-g-nylon (C).

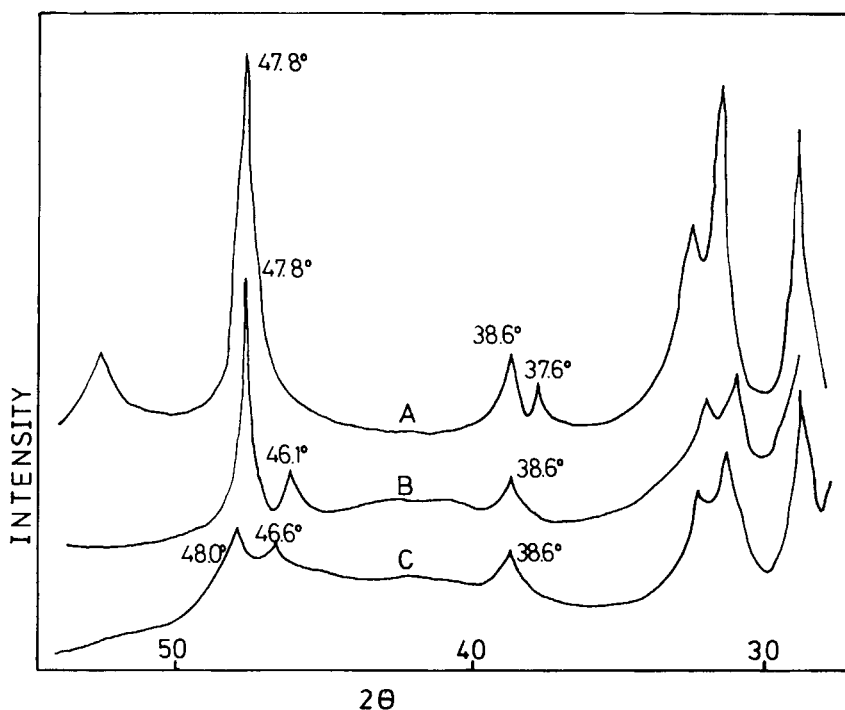


Fig. 12. X-ray diffraction intensity curve of  $\text{Cu}_x\text{S}$  powder (A),  $\text{Cu}_x\text{S}$ -AM-*g*-nylon (B), and  $\text{Cu}_x\text{S}$ -AN-*g*-nylon (C).

at  $2900\text{ cm}^{-1}$  and the  $-\text{CONH}_2$  band of primary amide group at  $1680\text{ cm}^{-1}$  can be seen. And in the case of AN-*g*-nylon, the  $-\text{CH}_2-$  band of vinyl group at  $2900\text{ cm}^{-1}$  and the band at  $2240\text{ cm}^{-1}$  related to the cyano group can be seen. The above results suggest that the grafting of AM or AN to the nylon films is carried out as expected.

Figure 12 shows the wide angle X-ray diffraction intensity profiles of  $\text{Cu}_x\text{S}$  powder,  $\text{Cu}_x\text{S}$ -AM-*g*-nylon and  $\text{Cu}_x\text{S}$ -AN-*g*-nylon.

In  $\text{Cu}_x\text{S}$  powder (A), the  $2\theta$  peaks were shown at  $47.8^\circ$ ,  $38.6^\circ$ , and  $37.6^\circ$ , and these peaks were known as the typical peaks of  $\text{Cu}_x\text{S}$ .<sup>17,18</sup> Meanwhile, in  $\text{Cu}_x\text{S}$ -AM-*g*-nylon (B), the  $2\theta$  peaks were shown at  $47.8^\circ$ ,  $46.1^\circ$  and  $38.6^\circ$  and, in  $\text{Cu}_x\text{S}$ -AN-*g*-nylon (C), the  $2\theta$  peaks were shown at  $48.0^\circ$ ,  $46.6^\circ$  and  $38.6^\circ$ .

The above finding can be explained by the fact that  $\text{Cu}_x\text{S}$  was introduced into the nylon film as expected. The difference of the  $2\theta$  peaks of  $\text{Cu}_x\text{S}$ -AM-*g*-nylon from those of  $\text{Cu}_x\text{S}$ -AN-*g*-nylon can be accounted for the difference of  $x$  in  $\text{Cu}_x\text{S}$  between both samples. The  $x$  value of  $\text{Cu}_x\text{S}$  will be calculated by energy dispersion X-ray analysis (EDAX) in our next paper.

#### Glass transition ( $T_g$ ) and Melting temperature ( $T_m$ )

Table I shows  $T_g$  and  $T_m$  of the original nylon, grafted nylon, and  $\text{Cu}_x\text{S}$ -treated nylon films. At the first glance  $T_m$  was not varied by grafting and by the  $\text{Cu}_x\text{S}$  introduction, but  $T_g$  of the grafted nylon decreased slightly. This

TABLE I  
 $T_g$  and  $T_m$  Measured by DSC

Film	$T_g$ ( $^{\circ}\text{C}$ )	$T_m$ ( $^{\circ}\text{C}$ )
Original nylon film	72	220
AM- <i>g</i> -nylon film	62	222
AN- <i>g</i> -nylon film	63	221
Cu <sub>x</sub> S-AM- <i>g</i> -nylon film	68	220
Cu <sub>x</sub> S-AN- <i>g</i> -nylon film	69	219

TABLE II  
 Electrical Conductivity of Individual Film<sup>a</sup>

Film	Conductivity (S/cm)
Original nylon film	$6.5 \times 10^{-12}$
AM- <i>g</i> -nylon film	$3.1 \times 10^{-12}$
AN- <i>g</i> -nylon film	$1.2 \times 10^{-12}$
Cu <sub>x</sub> S-AM- <i>g</i> -nylon film	$4.6 \times 10^{-3}$
Cu <sub>x</sub> S-AN- <i>g</i> -nylon film	$8.7 \times 10^{-3}$

<sup>a</sup>Samples dried at 105 $^{\circ}\text{C}$  for 2 h.

suggests that the grafting of AM or AN is carried out only in the amorphous region and the decrease of  $T_g$  is caused by the branching effect.

But  $T_g$  of Cu<sub>x</sub>S-treated nylon is higher than that of the grafted nylon, and this increase of  $T_g$  is due to the hindrance of free rotation caused by metal complex formation.

### Electrical Conductivity

Table II shows the conductivity of the original nylon, the grafted nylon, and the Cu<sub>x</sub>S-treated nylon films. Electrical conductivities of Cu<sub>x</sub>S-AM-*g*-nylon and Cu<sub>x</sub>S-AN-*g*-nylon were  $4.6 \times 10^{-3}$  and  $8.7 \times 10^{-3}$  s/cm, respectively, and the conductivity is higher by order of  $10^9$  than that of the original nylon film. This conductivity value is in the semiconductor region as Cu<sub>x</sub>S-treated PET films.<sup>4,5</sup> Dependence of the conductivity on temperature, the activation energy, and the conduction mechanism will be discussed in our later papers.

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