

Carbonization and Graphitization of Polyimide Films: Effect of Size of Leaving Group at Imidization

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ABSTRACT: Polyamide acid was prepared from pyromellitic dianhydride and *p*-phenylenediamine and was then reacted with NaH and various kinds of alkyl halides to transform into alkyl esters. The cast films were imidized as fixed on glass substrate to give polyimide films and were then carbonized by heating to 900°C. The electrical conductivity of the carbonized films decreased with the increase of the size of the leaving group at the imidization step. The carbonized films were further heated to 2800°C for graphitization. Their degrees of graphitization and orientation of the graphite crystallite as a function of weight loss at imidization were studied by X-ray diffraction measurement at room temperature and magnetoresistance measurement at liquid nitrogen temperature. Both measurements clearly indicate that the graphitized films prepared from polyamide acid alkyl ester have high degrees of graphitization. It was also made clear that the orientation of the graphitized films increased with the increase of the size of the leaving group at the imidization step. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1613–1620, 1998

Key words: polyimide film; carbonization; graphitization; graphitized film; orientation

INTRODUCTION

In recent years, pyrolysis of aromatic polymer films such as polyimide films at high temperature has been attracting much attention because high quality graphitized films maintaining their original film shapes can be obtained.^{1–8} We have been studying the effects of the chemical structure and orientation of the molecules in polyimide film on carbonization and graphitization.^{4,5,9,10} As a result, we found that when imidization of a polyamide acid film was carried out as fixed on a glass substrate, high quality graphitized film could be

obtained from the carbonized film by high temperature treatment.

The higher orientation of the molecules afforded by imidization as fixed on a glass substrate arises from the ordering of the polymer chains along the film surface, which is induced at imidization by losing water molecules and shrinking only in the direction perpendicular to the film surface. It is expected that utilization of polyamide acid alkyl ester as a precursor, instead of polyamide acid, would give a polyimide film with higher orientation of the molecules along the film surface, because polyamide acid alkyl ester imidizes by losing alcohols, which are larger molecules than water molecules.

We recently reported that polyimide films from the methyl ester of polyamide acid have high

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graphitizability, and orientation of the graphitized films increased with esterification ratio.¹¹ It is expected that the polyimide films utilizing polyamide acid derivatives having larger leaving groups as precursors will afford graphitized films of higher quality. In the present study, for the purpose of preparing highly oriented polyimide and also graphitized films, we prepared polyamide acid alkyl ester with various alkyl groups; the effect of the size of the leaving groups on the in-plane orientation of polyimide films and on the graphitizability was examined. The components of polyimide, pyromellitic dianhydride (PMDA) and *p*-phenylenediamine (PDA) were selected because polyimide molecules prepared from these components are rigid rods and the effect of orientation of the molecules can be characterized at various stages by measuring the tensile modulus at the polyimide films stage, electrical conductivity at the carbonized films stage, and X-ray diffraction and magnetoresistance at the graphitized films stage.

EXPERIMENTAL

Reagents

PDA was purified by repeated sublimation. PMDA was recrystallized from acetic anhydride. *N*-Methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure.

Preparation of Polyamide Acid Alkyl Ester

Polyamide acid alkyl esters were prepared by reacting polyamide acid with NaH and various kinds of alkyl halides: methyl iodide, allyl bromide, pentyl iodide, and octyl iodide. The preparation of methyl ester is shown below as a representative example.

Equimolar amounts of PDA (20.00 mmol, 2.1629 g) and PMDA (20.00 mmol, 4.3624 g) were reacted in 86.69 g of NMP for 12 h to give 7 wt % polyamide acid solution. The yellow solution was highly viscous. Viscosity of the polyamide acid was 1.80 dL/g at the concentration of 0.5 g/dL in NMP.

The 9.32 g of the 7 wt % solution was diluted with 23.30 g of NMP to give a 2 wt % solution. Sodium hydride (6.00 mmol, 144 mg) was added in small portions, and the mixture was stirred continuously for 6 h at room temperature. Methyl iodide (12.0 mmol, 1.00 mL) was then added dropwise and stirring was continued for 48 h at 15–

20°C. The solution was added into 1 L of 1 wt % HCl aqueous solution; after 30-min stirring, a yellow precipitate was filtered and washed with water and then with acetone to yield polyamide acid methyl ester as a yellow powder. The esterification ratio was calculated to be 79% from the ratio of the methyl proton (3.8 ppm) and phenyl proton (7.6–8.3 ppm) of ¹H-NMR. The viscosity of the polymer was 1.50 dL/g at a concentration of 0.5 g/dL in NMP. The yield of the methyl ester was 0.709 g and was calculated to be 102%, counting the esterification ratio of 79%.

Other alkyl substituents appeared on ¹H-NMR at 4.8–5.9 ppm for allyl, 0.8–1.6, and 4.2 ppm for pentyl, and 0.8–1.5 and 4.2 ppm for octyl substituents.

Preparation of Polyimide Films

A powder of polyamide acid alkyl ester was dissolved in NMP to give a 10 wt % solution that was cast on a glass plate followed by drying at 50°C for 15 h *in vacuo*. The cast films were then thermally treated as fixed on a glass substrate at 100, 200, and 300°C for 1 h each to give polyimide films. Some films, especially for the measurements of tensile properties, were further treated at 350°C for 30 min.

Carbonization of Polyimide Films

Polyimide films cut into 10 × 30 mm pieces were sandwiched between polished artificial graphite plates; they were heated to 900°C at a rate of 1°C/min by infrared radiation and kept at 900°C for 1 h in a flow of nitrogen. Black carbon films with a metallic luster were obtained.

Some carbonized films were further heated to 1800°C. The color of the heated films was black, and the appearance was between carbonized films pyrolyzed at 900°C and graphitized films pyrolyzed at 2800°C.

Graphitization

The carbonized films were sandwiched again between polished artificial graphite plates and heated to 2100°C at a rate of 2000°C/h; they were heated once at 2100°C for 1 h, then heated further to 2800°C at the same rate and then kept at that temperature for 30 min in a flow of argon. Silver graphitized films were obtained.

Table I Calculated Weight Loss at Imidization for PMDA/PDA Polyimide

Precursor	Calculated Weight Loss (%)
PAA	11.1
PAMe	18.1
PAAI	28.6
PAPn	37.8
PAOc	47.3

Measurements

The viscosities of polyamide acid and the alkyl ester were measured using an Ubbelohde viscometer at a concentration of 0.5 dL/g in NMP at $30.0 \pm 0.5^\circ\text{C}$. $^1\text{H-NMR}$ spectrum was obtained with FT-NMR spectroscopy on a Jeol JNM-GX270 using d_6 -DMSO as the solvent. The tensile properties of the polyimide films were measured using films cut into 3×50 mm portions at a crosshead speed of 1 mm/min. The electrical conductivity of the carbonized films was measured with the four-terminal method at room temperature.

X-ray diffraction of the graphitized films was measured employing a Rigaku Geigerflex RAD-1A with Cu $K\alpha$ radiation through an Ni filter combined with a scintillation counter. Each graphitized film was mounted on a specially designed sample holder for films. The 006 diffraction peak was measured to determine the interlayer d_{002} spacing using a thin specimen of highly oriented pyrolytic graphite (HOPG) with a flat cleaved surface as an outer standard. The d_{002} value of the HOPG standard was confirmed to be 0.3354 nm on the pulverized sample with an inner standard of high-purity silicon powder. To obtain informa-

tion on the degree of orientation, mosaic spread (MS) was measured for each graphitized film, which is defined by the full width at the half-maximum of the peak intensity recording of 002 diffraction plotted against rotation angle ϕ of the specimen.¹² The angle ϕ refers to the normal angle for the specimen surface at the diffraction angle giving the 002 intensity maximum.

The magnetoresistance measurement was carried out for graphitized films by immersing the specimen into liquid nitrogen as a function of strength and direction of the magnetic field. Two of the anisotropy ratios (r_{TL} and r_T) as a measure of the orientation degree of the graphite crystallite were obtained from the ratios $(\Delta\rho/\rho)_{TL\min}$ to $(\Delta\rho/\rho)_{\max}$ and $(\Delta\rho/\rho)_{T\min}$ to $(\Delta\rho/\rho)_{\max}$, respectively. $(\Delta\rho/\rho)_{TL\min}$ and $(\Delta\rho/\rho)_{T\min}$ are measured by directing the magnetic field parallel and perpendicular, respectively, to the current direction in the film surface. $(\Delta\rho/\rho)_{\max}$ is the maximum transverse magnetoresistance.

RESULTS AND DISCUSSION

Preparation of Polyamide Acid Alkyl Ester

Four kinds of alkyl esters of polyamide acid were prepared: methyl ester (PAMe), allyl ester (PAAI), pentyl ester (PAPn), and octyl ester (PAOc). The calculated weight loss at imidization is shown in Table I. They were obtained as yellow powders by the transformation of polyamide acid with NaH and then with alkyl halide as shown in Scheme 1. The reaction conditions and yields are summarized in Table II. Reactions were carried out at $15\text{--}20^\circ\text{C}$ because higher temperatures caused ge-

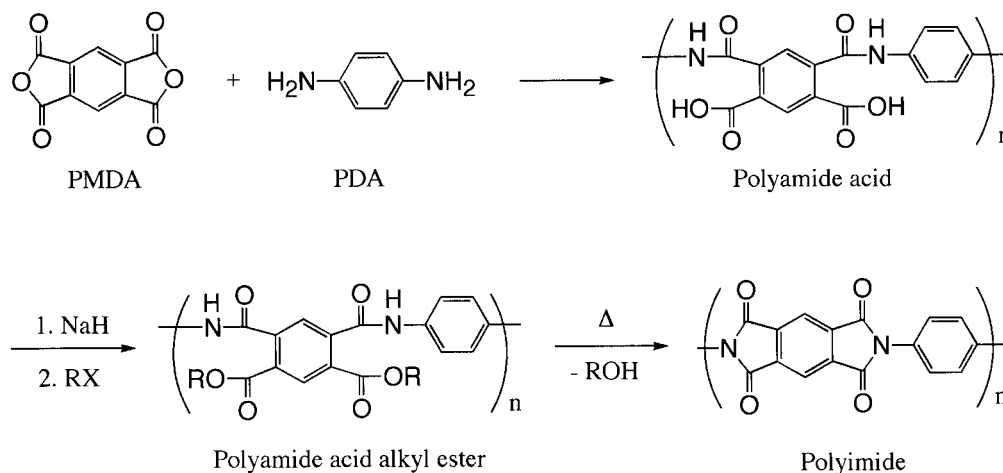
**Scheme 1** Transformation of polyamide acid with NaH and alkyl halide.

Table II Preparation of Polyamide Acid Alkyl Esters

Code	Alkyl Halide [mL (mmol)]	Yield [g (%)]	$\eta_{\text{red}}^{\text{a}}$ (dL/g)	Esterification Ratio (%)
PAMe	1.00 (12.0)	0.709 (102)	1.50	79
PAAl	1.03 (12.0)	0.833 (103)	1.45	98
PAPn	3.15 (24.0)	0.936 (100)	1.32	> 99
PAOc	4.48 (24.0)	1.091 (99)	1.33	> 99

The following amounts of reagents were used: polyamide acid, 0.653 g (2.00 mmol); NMP, 32.00 g; NaH, 144 mg (6.0 mmol). The reactions were carried out at 15–20°C for 48 h.

^a Viscosity of polyamide acid used was 1.80 dL/g in 0.5 g/dL of NMP.

lation. Twice the amount of alkyl halide was used in the case of pentyl or octyl iodide because the reaction with pentyl or octyl iodide was slower than that with methyl or allyl halide. Esterification ratios were calculated from the ratio of alkyl protons to phenyl protons of the ¹H-NMR measurement. Assuming 100% esterification, the proton ratios of the phenyl group and ester substituent were 3 : 5 for PAAl, 3 : 11 for PAPn, and 3 : 17 for PAOc. The esterification ratios were thus calculated to be above 98%, except for the methyl ester as shown in Table II. The reduced viscosity of the polymer was in the range of 1.32–1.50 dL/g and was moderately high due to the high reduced viscosity of the precursor polyamide acid of 1.80 dL/g. Cast films were easily prepared from the polymers.

Properties of Polyimide Films from Polyamide Acid Alkyl Ester

Polyimide films were prepared by thermally imidizing the cast films of polyamide acid alkyl ester

as fixed on glass substrates. Polyimide films were also prepared from polyamide acid similarly to examine the effect of alkyl substituents on the property of polyimides. The tensile properties of the polyimide films were measured to evaluate the in-plane orientation of the polyimide films. Films treated at 350°C were used as samples for the tensile measurements, considering the higher imidization temperature for the esterified polyamide acids. The results are summarized in Table III.

The tensile modulus of polyimide films derived from methyl ester was 8.3–8.6 GPa, and it was higher than that from polyamide acid (7.9–8.2 GPa). The high modulus of the polyimide films prepared from methyl ester suggests that higher orientation along the film surface was achieved; this might come from the elimination of the larger molecules of the methanol, rather than the elimination of water in the case of polyamide acid.

The larger leaving groups were expected to afford polyimide films with a higher modulus. The tensile modulus, however, tended to be lower with

Table III Tensile Modulus and Density of Polyimide Films

Precursor	ER (%)	Thickness (μm)	E (GPa)	σ (MPa)	Elongation (%)	d (g/cm ³)
PAA	0	22.0	8.2	78	1.26	1.5107
PAA	0	20.0	8.0	59	0.84	1.5107
PAA	0	20.0	7.9	74	1.01	1.5107
PAMe	79	19.2	8.6	48	0.67	1.4783
PAMe	79	15.0	8.4	31	0.46	1.4783
PAMe	79	15.5	8.3	43	0.66	1.4783
PAAl	98	17.0	8.4	99	1.57	1.4611
PAAl	98	20.3	8.3	42	0.53	1.4611
PAAl	98	17.5	7.9	84	1.39	1.4611
PAPn	> 99	20.3	7.8	65	0.96	1.4575
PAPn	> 99	18.0	7.8	27	0.39	1.4575
PAPn	> 99	20.0	7.7	41	0.61	1.4575
PAOc	> 99	20.0	—	—	—	1.4447

ER, esterification ratio. (—) Films were too brittle for the measurement.

Table IV Changes of Dimensions from Polyimide Films to Carbonized and Graphitized Films

Run	Polyimide Film			Carbon Film (Shrinkage) ^a			Graphite Film (Shrinkage) ^b			
	ER (%)	Thickness (μm)	Width (mm)	Length (mm)	Thickness (μm)	Width (mm)	Length (mm)	Thickness (μm)	Width (mm)	Length (mm)
PAA-1	0	20.7	10.09	29.78	11.0 (53)	9.0 (89)	26.5 (89)	—	—	—
PAA-2	0	21.7	9.86	29.74	10.5 (48)	8.9 (90)	26.5 (89)	—	—	—
PPA-3	0	20.7	9.86	30.18	—	8.9 (90)	26.8 (89)	6.6	9.2 (103)	27.7 (103)
PAA-4	0	21.0	10.15	29.78	—	9.1 (90)	26.5 (89)	4.6	9.4 (103)	27.6 (104)
PAMe-1	79	22.0	9.92	30.31	9.7 (44)	8.8 (89)	26.9 (89)	—	—	—
PAMe-2	79	23.7	10.01	30.18	11.3 (48)	8.9 (89)	26.7 (89)	—	—	—
PAMe-3	79	21.7	9.86	30.17	—	8.8 (89)	26.7 (89)	4.4	9.2 (105)	27.9 (103)
PAMe-4	79	21.7	10.01	29.78	—	8.9 (89)	26.4 (89)	4.4	9.3 (104)	27.4 (104)
PAAL-1	98	21.3	10.01	30.08	10.0 (47)	8.9 (89)	26.7 (89)	—	—	—
PAAL-2	98	22.7	10.16	30.26	8.0 (35)	9.0 (89)	26.7 (88)	—	—	—
PAAL-3	98	22.0	9.95	30.07	—	8.9 (88)	26.7 (89)	4.0	9.2 (105)	28.3 (106)
PAAL-4	98	20.7	9.80	30.14	—	8.7 (89)	26.7 (89)	3.5	9.2 (106)	27.8 (104)
PAPn-1	> 99	19.0	10.17	29.99	10.5 (55)	9.0 (89)	26.6 (89)	—	—	—
PAPn-2	> 99	21.0	10.17	30.06	8.3 (40)	9.0 (89)	26.7 (89)	—	—	—
PAPn-3	> 99	19.3	9.93	30.00	—	8.8 (89)	26.7 (89)	5.1	9.1 (103)	27.8 (104)
PAPn-4	> 99	20.0	10.01	30.06	—	8.9 (89)	26.7 (89)	5.7	9.3 (104)	28.0 (105)
PAOc-1	> 99	20.0	9.79	29.80	10.7 (54)	8.8 (90)	26.9 (90)	—	—	—
PAOc-2	> 99	19.7	10.08	29.74	9.2 (47)	8.9 (88)	26.5 (89)	—	—	—
PAOc-3	> 99	19.7	10.00	30.03	—	8.8 (88)	26.6 (89)	3.9	9.1 (103)	27.9 (105)
PAOc-4	> 99	20.7	9.79	29.74	—	8.8 (90)	26.5 (89)	5.4	9.1 (103)	28.0 (106)

ER, esterification ratio of polyamide acid.
^a Shrinkage ratio (%) from polyimide film.
^b Shrinkage ratio (%) from carbon film.

the larger leaving groups: 7.9–8.4 GPa for the allyl ester and 7.7–7.8 GPa for the pentyl ester as shown in Table III. Polyimide films from octyl ester were too brittle for the tensile measurements.

The reason for the lowered modulus in the case of the larger leaving group was thought to be that the packing of the polymer chains becomes loose when larger molecules volatilize from the films,

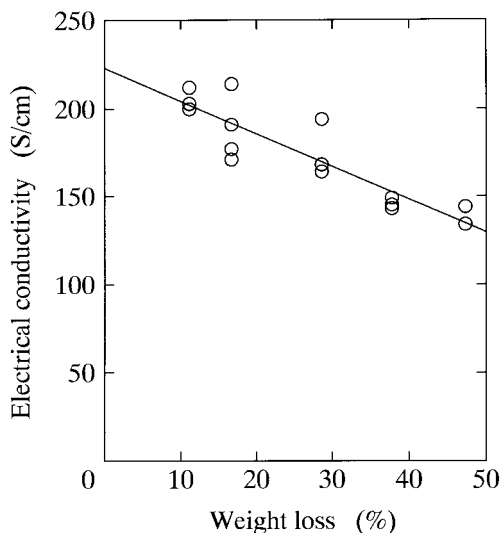


Figure 1 Electrical conductivity of carbonized films treated at 900°C utilizing polyamide acid alkyl ester.

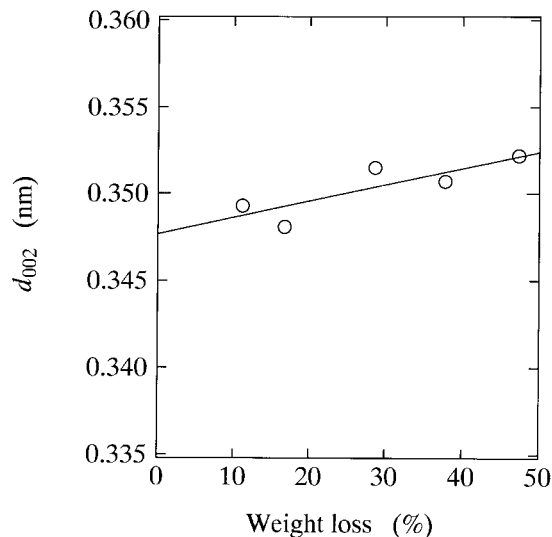


Figure 2 The d_{002} of carbonized films treated at 900°C utilizing polyamide acid alkyl ester.

Table V Dimensions and Properties of Carbonized Films Pyrolyzed in 1800°C

Precursor	Thickness (μm)	Width (mm)	Length (mm)	Conductivity (S/cm)	d_{002} (nm)	MS ($^{\circ}$)
PAA	3.8	9.2	27.5	1324	0.3436	16.5
PAMe	3.2	9.2	27.4	1426	0.3488	16.4
PAAI	3.0	9.0	27.6	1320	0.3448	15.7
PAPn	5.4	9.2	27.0	1353	0.3446	15.2
PAOc	1.2	9.2	27.6	1282	0.3469	17.9

which was confirmed by the density measurement of polyimide film as shown in Table III.

Preparation and Characterization of Carbonized Films

Polyimide films obtained from polyamide acid alkyl esters were carbonized by treating at 900°C. In every case, black carbonized films with a metallic luster were obtained. All the films shrunk with the same ratio in the width and length of the films (88–90%) but shrunk more in the thickness direction (35–55%) as shown in Table IV. The carbonized films were brittle, and the thickness was not measured for the films to be graphitized.

The carbonized films were characterized by electrical conductivity and X-ray analyses. It was observed that the electrical conductivity of the carbonized films was lowered with the increase of the leaving groups as shown in Figure 1. It was also observed that d_{002} slightly increased with the increase of the leaving groups as shown in Figure

2. These results suggest that carbonized films obtained from polyamide acid alkyl ester with larger leaving groups have lower crystallinity. Apparently the lower density of the polyimide films from the larger leaving groups has a great influence on the carbonized films.

After the pyrolysis at 1800°C, the carbonized films were also characterized by electrical conductivity and X-ray analyses. The results are shown in Table V and Figures 3–5. It can be seen that there are much smaller differences in the values between the carbonized films pyrolyzed at 1800°C in comparison to those pyrolyzed at 900°C.

Preparation and Characterization of Graphitized Films

The carbonized films were further heated to 2800°C to give graphitized films. As shown in Table IV, the thickness of each carbonized film decreased considerably after graphitization but the width and length elongated, suggesting that a

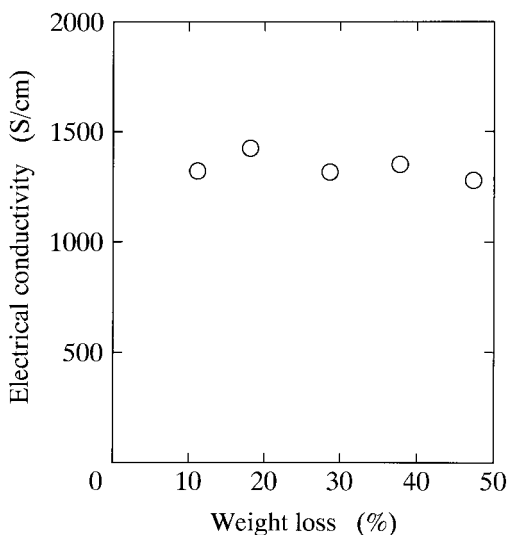


Figure 3 Electrical conductivity of carbonized films treated at 1800°C utilizing polyamide acid alkyl ester.

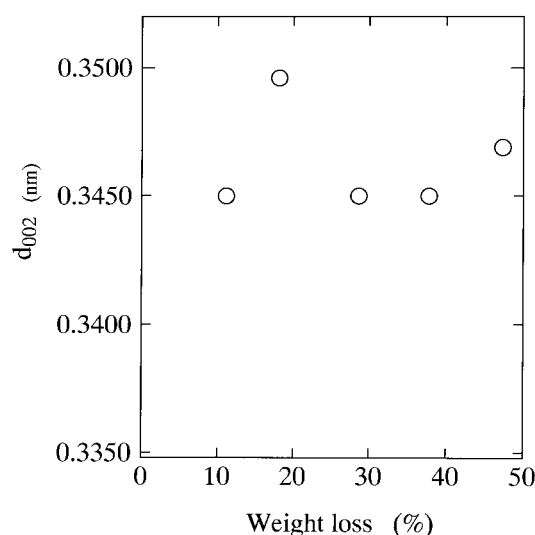


Figure 4 The d_{002} of carbonized films treated at 1800°C utilizing polyamide acid alkyl ester.

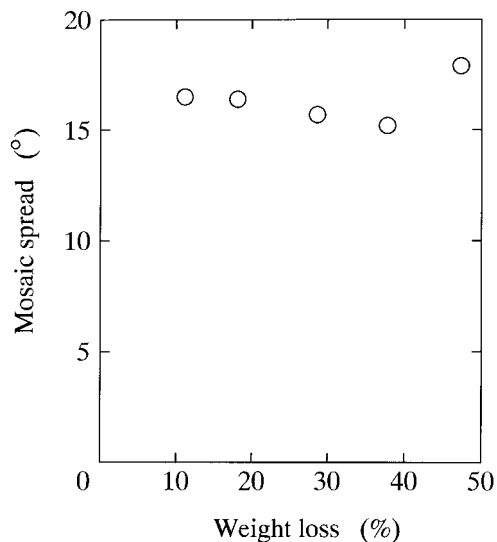


Figure 5 Mosaic spread of carbonized films treated at 1800°C utilizing polyamide acid alkyl ester.

high degree of orientation along the film surface was achieved for each graphite film. Degrees of graphitization and orientation of the graphite crystallites in the graphitized films were examined by X-ray diffraction and magnetoresistance measurements. The results are summarized in Table VI.

X-ray Diffraction Measurement

For all the graphitized films, the 006 diffraction peaks due to $K_{\alpha 1}$ and $K_{\alpha 2}$ were separated very well as shown in Figure 6 for the graphitized film prepared from polyamide acid methyl ester as an example, indicating that graphite crystallites are well organized.

The values of d_{002} , an indication of the graphitizability, were calculated to be 0.3357 nm for all the graphitized films examined. This is close to

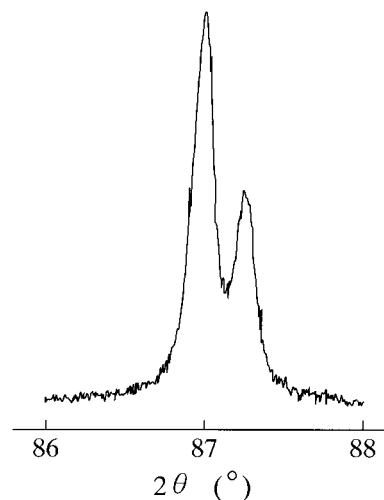


Figure 6 The 006 diffraction pattern of graphitized film prepared from polyamide acid methyl ester (83% esterification ratio).

that of natural graphite (0.3354 nm), suggesting a high degree of graphitization for the films.

As an indication of orientation, MS was obtained. The MS of the graphitized film prepared from polyamide acid alkyl ester having larger leaving groups is narrower than that of the smaller leaving groups as shown in Figure 7, indicating that a high degree of orientation of the graphite crystallites was achieved for the graphitized films with larger leaving groups.

Magnetoresistance Measurement

The values of $(\Delta\rho/\rho)_{\max}$ in a magnetic field of 1 T at liquid nitrogen temperature, a measure of degree of graphitization, were between 130.5 and 175.0% for all the graphitized films, which suggests that the graphitizability of the carbonized films examined was quite high. As shown in Figure 8, $(\Delta\rho/\rho)_{\max}$ was almost the same, irrespec-

Table VI X-ray and Magnetoresistance Measurements of Graphitized Films Pyrolyzed at 2800°C

Precursor	d_{002} (nm)	MS (°)	$(\Delta\rho/\rho)_{\max}$ (%)	r_{TL}	r_T
PAA	0.3357	8.4	154.4	0.065	0.082
PAMe	0.3355	9.2	143.0	0.058	0.054
PAMe	0.3357	8.5	146.7	0.060	0.052
PAAl	0.3357	7.5	130.5	0.062	0.069
PAAl	0.3357	8.1	131.6	0.055	0.061
PAPn	0.3357	8.4	164.4	0.053	0.060
PAPn	0.3357	7.3	175.0	0.028	0.032
PAOc	0.3357	6.7	139.4	0.033	0.048

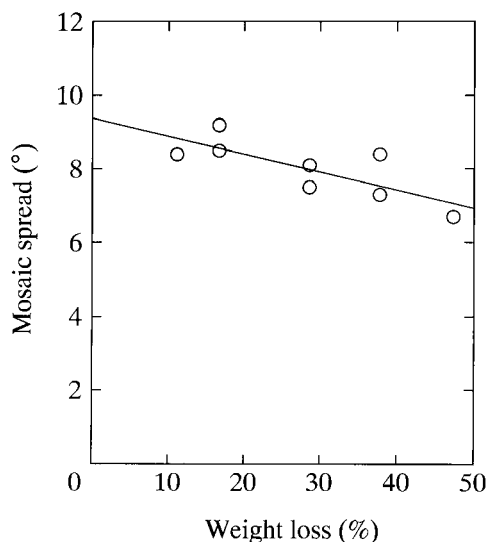


Figure 7 Mosaic spread of graphitized films utilizing polyamide acid alkyl ester.

tive of the size of the leaving groups. The results indicate that the degree of graphitization of the graphitized film was not promoted very much by esterification.

On the other hand, the anisotropy ratios, r_T and r_{TL} , decreased with the increase of the leaving group as shown in Figure 9, indicating that a higher orientation of the graphitized film was achieved with the larger leaving group at imidization.

In conclusion, it was made clear from the measurements of X-ray and magnetoresistance that

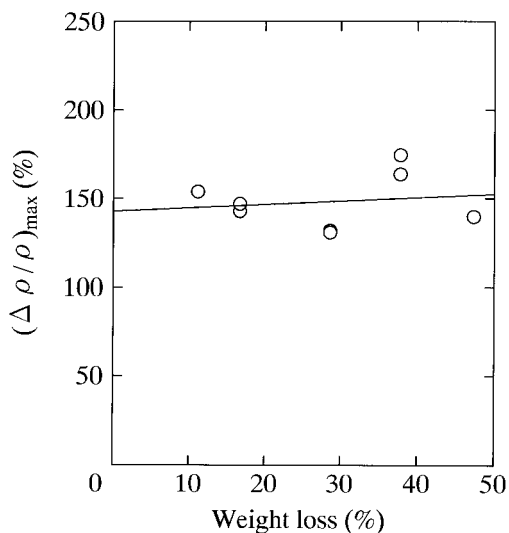


Figure 8 $(\Delta\rho/\rho)_{\max}$ of graphitized films utilizing polyamide acid alkyl ester.

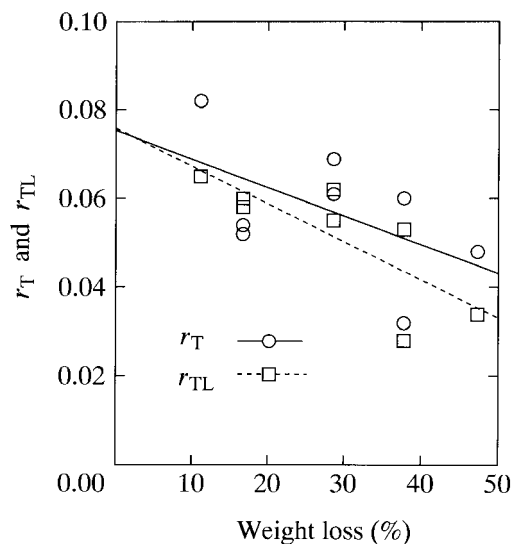


Figure 9 r_{TL} and r_T of graphitized films utilizing polyamide acid alkyl ester.

polyimide films from polyamide acid alkyl ester have high graphitizability. Above all, it was found out from the MS and anisotropy ratios of the magnetoresistance measurement that the orientation of the graphitized films increased with the increase of the leaving group.

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