Carbonization and Graphitization of Polyimide Films: Polyamide Acid Methyl Ester of PMDA/PDA as a Precursor

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SYNOPSIS

Polyamide acid was prepared from pyromellitic dianhydride (PMDA) and p-phenylene-diamine (PDA) and was then reacted with NaH and methyl iodide to transform into methyl ester having various degrees of esterification. Polyamide acid methyl ester was also prepared by the polymerization between PDA and acid chloride of half-ester of PMDA. The cast films were imidized as fixed on glass substrate to give polyimide films having slightly higher tensile moduli than those from polyamide acid, suggesting that higher orientation along the film surface was achieved. It should be noted that the polyimide films prepared by the latter method from the meta-rich configuration had considerably low modulus. The poly-imide films were then carbonized by heating to 900°C, and the electrical conductivity of the carbonized films was measured at room temperature. It was shown that the carbonized films from methyl ester have higher electrical conductivity than the films from corresponding polyamide acid. The carbonized films were further heated to 2800°C for graphitization, and their degrees of graphitization and orientation of the graphite crystallite as a function of esterification ratio were studied by x-ray diffraction measurement at room temperature and magnetoresistance measurement at liquid nitrogen temperature. Both measurements clearly indicate that the graphite films prepared from polyamide acid methyl ester have high degrees of graphitization and orientation. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, pyrolysis of aromatic polymer films such as polyimide films at high temperature has been attracting much attention because high-quality graphite films retaining 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 graphite 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 to the direction perpendicular to the film surface. Polyamide acid alkyl ester imidizes by losing alcohols, larger molecules than water molecules, which give larger shrinkage at imidization than that of polyamide acid. 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, when it is imidized as fixed on a glass substrate.

In the present study, we prepared polyamide acid methyl ester with various esterification ratios, and the cast film was imidized, followed by carbonization and graphitization. Components of polyimide, pyromellitic dianhydride (PMDA), and p-phenylene-

diamine (PDA) were selected because polyimide molecules prepared from these components are rigid rods. The effect of orientation of the molecules was characterized at various stages, by measuring tensile modulus at the stage of polyimide films, by electrical conductivity at the stage of carbonized films, and by x-ray diffraction and magnetoresistance at the stage of graphite films.

EXPERIMENTAL

Reagents

PDA was purified by sublimation. PMDA was recrystallized from acetic anhydride. N-methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure. 2,5-Dicarbomethoxyterephthaloyl chloride was prepared according to the procedure of Nishizaki and Morikawa.[11] For the preparation of acid chloride, oxalyl chloride was also used along with thionyl chloride.

Preparation of Polyamide Acid Methyl Ester by the Reaction of 2,5-Dicarbomethoxyterephthaloyl Chloride (Method A)

Polyamide acid methyl ester was prepared by modifying the method developed by Nishizaki and Morikawa.[11]

PDA (0.4324 g, 3.998 mmol) was dissolved in NMP (17.09 g) under nitrogen atmosphere. 2,5-Dicarbomethoxyterephthaloyl chloride (1.2769 g, 4.002 mmol) was added into the solution, keeping the flask at −10°C. Reaction was continued for 12 h at room temperature to give yellow solution, which was poured into 500 mL of distilled water. Precipitate was filtered, washed with water, and dried in vacuo at room temperature for 12 h to give 1.49 g (95%) of yellow powder.

Preparation of Polyamide Acid Methyl Ester by the Reaction of Polyamide Acid with Sodium Hydride and Methyl Iodide (Method B)

Polyamide acid methyl ester with various degrees of esterification was prepared by reacting polyamide acid with NaH and methyl iodide. The degree of esterification was controlled by the ratio of the reagents. A representative example is shown below.

Equimolar amount 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 in NMP. The yellow solution was

highly viscous. Viscosity of the polyamide acid was 2.0 dL/g at the concentration of 0.5 g/dL in NMP.

The 13.98 g of the 7 wt % solution was diluted with 34.96 g of NMP to give 2 wt % solution. Sodium hydride (7.20 mmol, 173 mg) was added in small portions and then stirred for 12 h. Methyl iodide (14.4 mmol, 0.90 mL) was then added dropwise and stirred for 48 h. The solution was added into 1 L of 1 wt % HCl aqueous solution and, after stirring 30 min, yellow precipitate was filtered and was washed with water to give polyamide acid methyl ester as yellow powder. Yield of the powder was 1.05 g (100%). Esterification ratio was calculated to be 78% from the ratio of methyl proton (3.8 ppm) and phenyl proton (7.6–8.3 ppm) of ^{1}H-NMR. The viscosity of the polymer was 1.70 dL/g at a concentration of 0.5 g/dL in NMP.

Preparation of Polyimide Films

Polyamide acid methyl ester powder was dissolved in NMP to give 10 wt % solution that was cast on glass plates followed by drying at 50°C for 15 h in vacuo. The cast films were thermally treated, as fixed on a glass substrate, at 100, 200, and then at 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.

Polyimide films were also prepared from polyamide acid similarly to examine the effect of methyl ester on the property of polyimides.

Carbonization of Polyimide Films

Polyimide films prepared by the method B were carbonized. The polyimide films cut into 10 × 30 mm were sandwiched between polished artificial graphite plates and were heated up to 900°C at a rate of 1°C/min by IR radiation and kept at 900°C for 1 h in a flow of nitrogen. Black carbon films having metallic luster were obtained.

Graphitization

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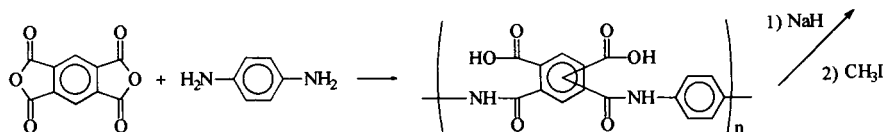
Measurements

Viscosity of polyamide acid and its methyl ester were measured using Ubbelohde viscometer at a concen-

Method A
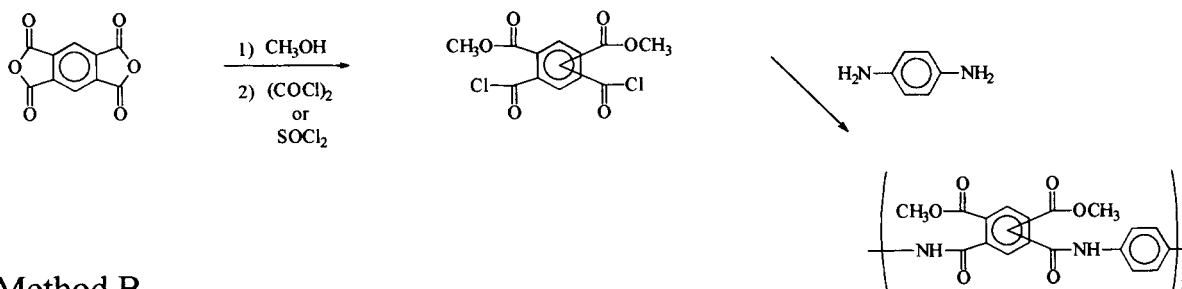
Method B

Scheme 1.

tration of 0.5 g/dL in NMP at 30.0 ± 0.5°C. ^{1}H-NMR spectrum was obtained with JEOL JNM-GX270 FT-NMR Spectroscopy, using d_6-dimethyl sulfoxide or $CDCl_3$ as a solvent. Tensile properties of polyimide films were measured using films cut into 3 × 50 mm at a cross head speed of 1 mm/min. The electrical conductivity of carbonized films was measured with four-terminal method at room temperature.

X-ray diffraction of the graphitized films was measured using Rigaku Geigerflex RAD-1A with Cu Kα radiation through Ni filter combined with a scintillation counter. Each graphite film was mounted on a specially designed sample holder for films. The 006 diffraction peak was measured to determine the interlayer spacing d_{002}, 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 inner standard of high-purity silicon powder. To obtain information on degree of orientation, mosaic spread 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 is referred to the normal to the specimen surface at the diffraction angle, giving the 002 intensity maximum.

The magnetoresistance measurement was carried out for graphitized films, immersing the specimen in liquid nitrogen, as a function of strength and direction of the magnetic field. A couple of the anisotropy ratios r_{TL} and r_T as a measure of orientation degree of the graphite crystallite were obtained from

the ratios $(\Delta\rho/\rho)_{TLmin}$ to $(\Delta\rho/\rho)_{max}$ and $(\Delta\rho/\rho)_{Tmin}$ to $(\Delta\rho/\rho)_{max}$, respectively. $(\Delta\rho/\rho)_{TLmin}$ and $(\Delta\rho/\rho)_{Tmin}$ 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 methyl ester

Methyl ester of polyamide acid was prepared by two different methods: by the polymerization of half ester of acid dianhydride monomer with diamine (method A) and by the transformation from polyamide acid (method B) as shown in Scheme 1.

Method A gave polyamide acid methyl ester having moderate solution viscosity as shown in Table I. The solubility of the polyamide acid methyl ester, however, depends on the para-meta (or *trans-cis*) ratio of the polyamide acid methyl ester. The solubility of meta-rich polymers is excellent, but para-rich polymers dissolved only to the limited amount. The low molecular weight and poor solubility of the para-rich polymer made the formation of cast films difficult.

Method B gave polyamide acid methyl ester having various esterification ratios (28–83% from ^{1}H-NMR measurement) as shown in Table II. The esterification ratio can be controlled by the ratio of NaH and CH_3I to polyamide acid as is clearly seen in runs 1–4 in Table II. Reaction time is not necessary to be long, and a reaction of 3–12 h is sufficient as seen from runs 6 and 7 in Table II. The

Table I Preparation and Properties of Polyamide Acid Methyl Ester by Method A

	Acid Chloride		PDA		Polyamide Acid Methyl Ester	
Run	Para : Meta	g (mmol)	g (mmol)	Solvent	Yield[a] (g)	η_{red} (dL/g)
1	100 : 0	1.5955 (5.000)	0.5407 (5.000)	NMP 20 mL/THF 4 mL[b]	2.14 (75)	0.57
2	22 : 78	1.3392 (3.002)	0.3248 (3.004)	NMP 11.60 g[c]	0.99 (55)	0.22
3	60 : 40	1.5955 (5.000)	0.5407 (5.000)	NMP 19.23 g[c]	1.68 (93)	0.37
4	26 : 74	1.2769 (4.002)	0.4324 (3.998)	NMP 17.09 g	1.49 (95)	0.41

[a] Values in parentheses are percents.
[b] Pyridine (0.79 g) was added as acid acceptor.
[c] Lithium chloride (0.3 g) was added.

ratio of para/meta of the polymer obtained by the method B was found to be 50 : 50 from the ^{1}H-NMR measurement. Solubility of the polymer to organic solvents was excellent. The solution viscosity of the polymer was in the range of 0.7–1.7 dL/g and moderately high due to the high solution viscosity of the precursor polyamide acid of 2.0 dL/g. The lower solution viscosity of the ester is supposed to come from the lower interaction of polymer chains by the esterification and also small amount of chain scission. Cast films can be easily prepared from the polymer obtained by the method B.

Properties of Polyimide Films From Polyamide Acid Methyl Ester

Polyimide films were prepared by thermally imidizing the cast films of polyamide acid methyl ester from the methods A and B as fixed on glass substrates. Polyimide films were also prepared from

polyamide acid similarly to examine the effect of methyl ester on the property of polyimides. The tensile properties of the polyimide films are summarized in Table III.

The films prepared by the method A have considerably low tensile modulus that should come from low imidization ratio even after 350°C treatment. The less rigid configuration of meta-rich precursor polymer might hinder high degree of imidization which require to be rod-like in the solid state.

The films of polyamide acid methyl ester from the method B, on the other hand, have higher modulus than the polyimide films from polyamide acid. The high modulus of the polyimide films prepared from esterified polymer suggests that higher orientation along the film surface was achieved, which might come from the elimination of larger molecule, methanol, than the elimination of water in the case of polyamide acid.

Table II Preparation and Properties of Polyamide Acid Methyl Ester by Method B

	Polyamide Acid		NMP	NaH	CH_3I	Time[b]	Polyamide Acid Methyl Ester		
Run	g (mmol)	dL/g[a]	(g)	mg (mmol)	mL (mmol)	(h)	g (%)[c]	dL/g[a]	E.r. (%)[d]
1	0.979 (3.00)	1.95	47.97	43 (1.80)	0.23 (3.6)	48	0.91 (91)	0.79	28
2	0.979 (3.00)	1.95	47.97	86 (3.60)	0.45 (7.2)	48	0.99 (98)	0.90	38
3	0.979 (3.00)	1.95	47.97	130 (5.40)	0.68 (10.8)	48	1.04 (101)	1.26	54
4	0.979 (3.00)	1.95	47.97	173 (7.20)	0.90 (14.4)	48	1.05 (100)	1.70	78
5	0.653 (2.00)	1.95	32.00	144 (6.00)	1.00 (16.0)	24	0.67 (96)	1.19	83
6	0.653 (2.00)	2.00	32.00	150 (6.25)	1.00 (16.0)	3	0.68 (98)	0.71	78
7	0.653 (2.00)	2.00	32.00	150 (6.25)	1.00 (16.0)	12	0.71 (102)	0.81	82

[a] Reduced viscosity.
[b] Reaction time.
[c] Yield (%) was calculated based on the obtained esterification ratio.
[d] Esterification ratio.

Table III   Tensile Properties of PMDA/PDA Polyimide Films[a]

	Precursor				Tensile Properties		
Type	E.r. (%)	Viscosity (dL/g)	Stretching	E' (GPa)	σ (MPa)	Elongation (%)
Polyamide acid	0	0.98	No	4.7	31	0.74
Polyamide acid		0.98	No	4.9	40	0.95
Polyamide acid		0.98	No	5.4	22	0.39
Polyamide acid		0.98	No	7.6	33	0.55
Polyamide acid	0	0.98	On glass	7.1	24	0.39
Polyamide acid		0.98	On glass	7.7	33	0.44
Polyamide acid		1.25	On glass	7.9	74	1.01
Polyamide acid		1.25	On glass	8.2	78	1.26
Methyl ester (method A)	100	0.41	On glass	3.0	23	0.84
Methyl ester (method A)		0.41	On glass	3.6	18	0.17
Ethyl ester (method A)	100	0.40	On glass	4.7	65	1.55
Ethyl ester (method A)		0.40	On glass	4.8	12	0.31
Methyl ester (method B)	54	1.26	On glass	7.8	44	0.66
Methyl ester (method B)		1.26	On glass	8.2	36	0.48
Methyl ester (method B)		0.66	On glass	8.9	17	0.19
Methyl ester (method B)		0.66	On glass	9.1	19	0.24
Methyl ester (method B)	78	1.70	On glass	8.5	54	0.66
Methyl ester (method B)		1.70	On glass	8.6	34	0.44
Methyl ester (method B)		1.70	On glass	9.0	35	0.43
Methyl ester (method B)		0.71	On glass	9.0	46	0.56

[a] Imidized at 350°C.
[b] E.r. = esterification ratio.

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

		Polyimide Film			Carbon Film[b]			Graphite Film[c]		
Run	E.r.[a] (%)	Thickness (μm)	Width (mm)	Length (mm)	Thickness (μm)	Width (mm)	Length (mm)	Thickness (μm)	Width (mm)	Length (mm)
1	0	19.8	9.5	29.8	12.9 (65)	8.5 (89)	26.6 (89)	—	—	—
2	0	20.8	10.0	29.8	—	9.0 (90)	26.7 (90)	7.9	9.1 (101)	27.5 (103)
3	0	22.4	10.1	29.8	—	9.0 (89)	26.6 (89)	6.9	9.3 (103)	27.5 (103)
4	28	18.4	10.0	29.5	11.1 (60)	8.6 (86)	26.3 (89)	—	—	—
5	28	13.8	10.2	29.9	—	9.0 (88)	26.1 (87)	4.6	9.3 (103)	27.1 (104)
6	28	21.8	10.0	29.5	—	9.0 (90)	26.2 (89)	5.9	9.3 (103)	27.2 (104)
7	38	15.2	9.7	29.5	9.2 (61)	8.7 (90)	26.3 (89)	—	—	—
8	38	22.4	10.0	29.6	—	9.0 (90)	26.3 (89)	6.4	9.2 (102)	27.4 (104)
9	54	24.8	9.9	29.8	11.5 (46)	8.8 (89)	26.3 (88)	—	—	—
10	54	21.0	9.9	29.8	—	8.9 (90)	26.5 (89)	5.5	9.3 (105)	27.6 (104)
11	78	24.4	9.9	29.7	12.2 (50)	8.8 (89)	26.6 (90)	—	—	—
12	78	23.2	9.9	29.9	—	8.8 (89)	26.6 (89)	7.0	9.1 (103)	27.6 (104)
13	83	18.0	10.0	29.9	12.2 (68)	9.0 (90)	26.7 (89)	—	—	—
14	83	18.2	9.8	29.9	—	8.7 (89)	26.6 (89)	6.5	9.0 (103)	27.8 (105)

[a] Esterification ratio of polyamide acid.
[b] Values in parentheses are shrinkage ratios in % from polyimide film.
[c] Values in parentheses are shrinkage ratios in % from carbon film.
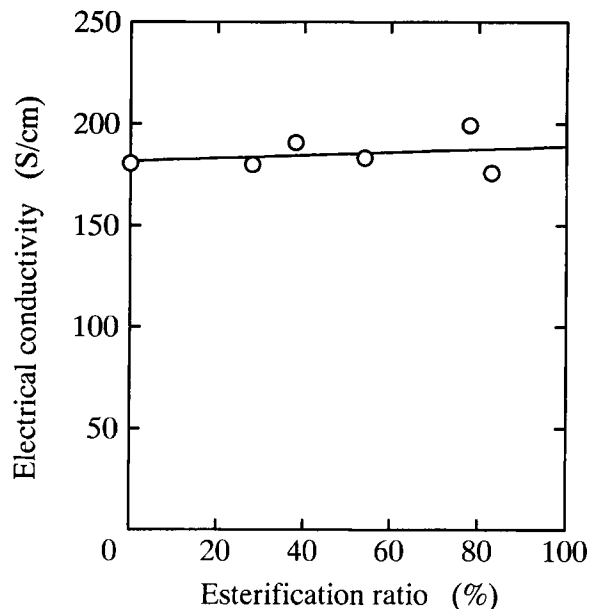
Figure 1 Electrical conductivity at room temperature for carbonized films as a function of esterification ratio.

Preparation and Characterization of Carbonized Films

Polyimide films prepared by the method B were carbonized because higher orientation of the molecules along the film surface was suggested by the tensile modulus measurement. All the films shrunk with the same ratio in width and length of the films (88–90%) but shrunk much in the thickness direction
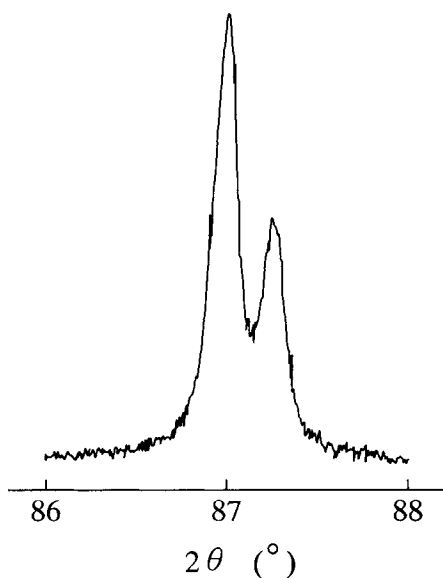
Figure 2 Diffraction pattern of 006 on graphitized film with esterification ratio of 83%.
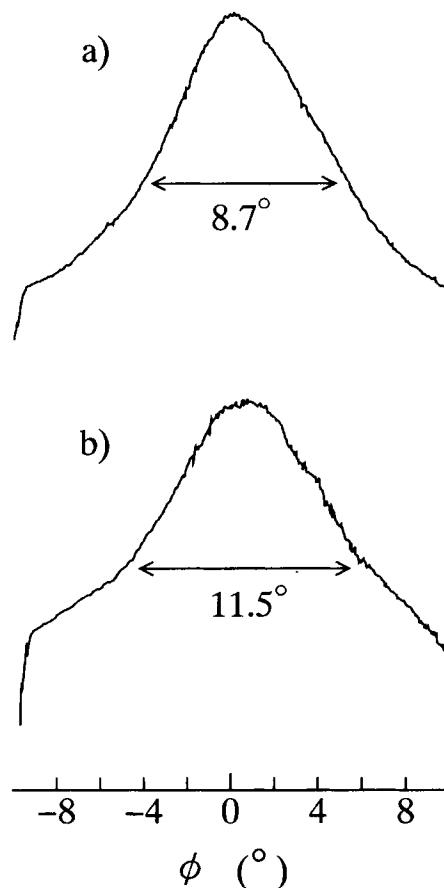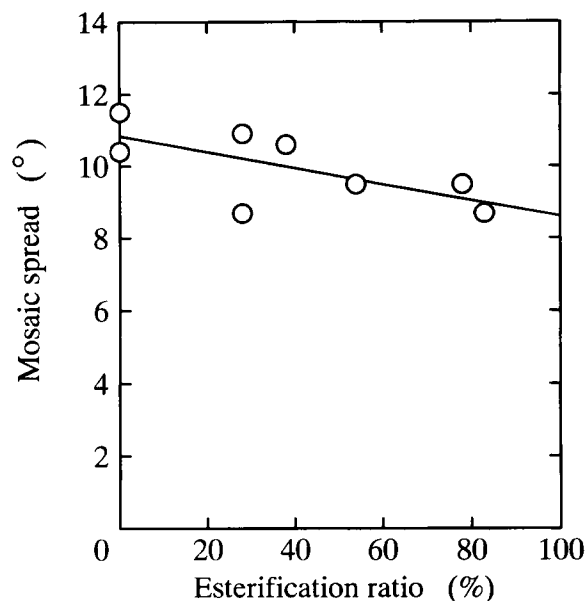

Figure 3 Intensity recording of 002 for graphitized films. (a) Esterification ratio of 83%; (b) without esterification.

(46–54%) as shown in Table IV. The carbonized films were brittle, and the thickness was not measured for the films to be graphitized.

The electrical conductivity of the carbonized films is plotted as a function of esterification ratio in Figure 1. The films showed excellent electrical conductivity (180–200 S/cm). There is a tendency that the carbonized films prepared from polyamide acid with higher degree of esterification have higher electrical conductivity, which is in accord with the modulus at the stage of polyimide. Although the conditions are not exactly the same, the comparison with the previous paper[10] suggests that the carbonized films obtained in the present study show the electrical conductivity corresponding to 20% cold-drawing.

Preparation and Characterization of Graphitized Films

The carbonized films were further heated up to 2800°C to give graphitized films. As shown in Table IV, thickness of each carbonized film decreased con-
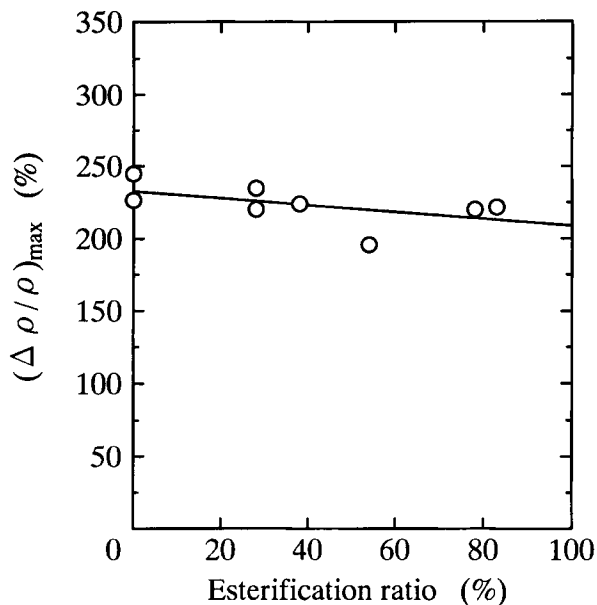
Figure 4 Mosaic spread for graphitized films as a function of esterification ratio.

Figure 5 Values of $(\Delta\rho/\rho)_{max}$ measured at liquid nitrogen temperature in a field of 1 T for graphitized films as a function of esterification ratio.

siderably after graphitization, whereas the width and length elongated, suggesting that high degree of orientation along the film surface was achieved for each graphite film. Degrees of graphitization and orientation of the graphite crystallite in the graphitized films were examined by X-ray diffraction and magnetoresistance measurements.

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 2, for the graphitized film prepared from polyamide acid methyl ester with 83% esterification ratio (run 14 in Table IV) as an ex-

ample, 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, which is close to that of natural graphite, 0.3354 nm, suggesting high degree of graphitization for the films.

Mosaic spread of the graphitized film prepared from polyamide acid methyl ester of higher esterification ratio is narrower than that of the lower esterification ratio as shown in Figures 3 and 4, indicating that high degree of orientation of the graphite crystallites is achieved for the graphitized films with higher esterification ratio.

Table V   Magnetoresistance Parameters Measured at Liquid Nitrogen Temperature in a Field of 1 T

Sample E.r.[a] (%)	$(\Delta\rho/\rho)_{max}$	$(\Delta\rho/\rho)_{TLmin}$	$(\Delta\rho/\rho)_{Tmin}$	r_{TL}	r_T
0	226.7	17.8	18.5	0.079	0.082
0	244.7	19.1	18.8	0.078	0.077
28	234.9	17.4	17.8	0.074	0.076
28	220.5	15.7	16.4	0.071	0.074
38	223.8	13.0	14.5	0.058	0.065
54	195.9	13.3	13.0	0.068	0.066
78	220.3	11.8	12.8	0.058	0.058
83	221.8	13.0	11.2	0.059	0.050

[a] E.r. = esterification ratio.
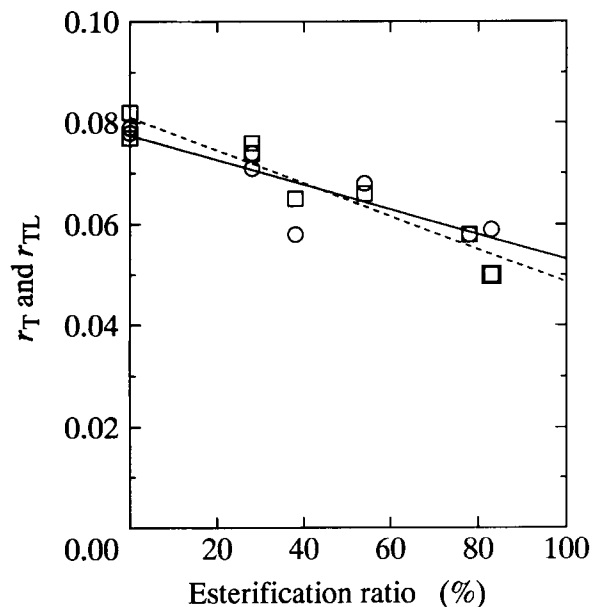
Figure 6 Ratios, r_T and r_{TL}, measured at liquid nitrogen temperature in a field of 1 T for graphitized films as a function of esterification ratio. $\bigcirc$, r_T; $\square$, r_{TL}.

Magnetoresistance Measurement

The results of the magnetoresistance measurements are summarized in Table V. For all the graphite films, the values of $(\Delta\rho/\rho)_{max}$ in a magnetic field of 1 T at liquid nitrogen temperature are between 195.9 and 244.7%, which roughly corresponds to that for the graphite film obtained from a high modulus polyimide film prepared via polyamide acid gel by the heat treatment at 2800°C.[12] Accordingly, the graphitizability of each of the present carbonized films is quite high. As shown in Figure 5, $(\Delta\rho/\rho)_{max}$, a measure of degree of graphitization tends to decrease with esterification ratio. The results are against our expectation and indicate that the degree of graphitization of the graphitized film is not promoted by esterification.

On the other hand, the anisotropy ratios r_T and r_{TL}, measures of the degree and mode of orientation of graphite layers along the film surface, decreased with esterification ratio as shown in Figure 6, in-

dicating that higher orientation of the graphitized film is achieved with higher esterification of the polyimide film.

In conclusion, it was made clear from the measurements of X-ray and magnetoresistance that polyimide films from polyamide acid methyl ester have high graphitizability. Especially, it was found out from the mosaic spread and magnetoresistance measurements that the orientation of the graphitized films increased with esterification ratio. It is expected that the polyimide films utilizing polyamide acid derivatives having larger leaving groups as precursors will afford graphite films of higher quality. We are currently studying the graphitization of them.

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