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Ion beam-induced positive imaging of polyimide via two step imidization

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Abstract

The preparation of ion track membranes of thermally stable polyimide films has been performed by ion beam irradiation of partially imidized polyamic acid (PAA) films followed by alkaline etching and final imidization. No discernible positive hole patterns were observed on the irradiated films of partially imidized PAA containing sulfonyl linkages, although sulfonyl group is known to be highly sensitive to ion beams. In contrast, positive hole patterns appeared on the irradiated films of the partially imidized PAA with 68–89% imidization degrees that contains sulfonyl linkages along with a methylene group in the main chain. The most contrasty hole patterns with 0.3 μm diameter were observed on the irradiated PAA films of 89% imidization degree. The irradiated PAA film with the hole patterns was then transformed to the corresponding polyimide film with curing at 350 °C for 1 h. From the structural comparison of the polyimides, the possible mechanism for the hole pattern formation is suggested.

Keywords: Ion track membrane; Partially imidized polyamic acid; Ion beam irradiation

1. Introduction

Nanoscopic patterning of organic thin films using ion and electron beams is expected to play a crucial role in fabrication of electronic devices of the next generation, since these beams are able to be focused to a diameter in nanometer scale and scanned at high speeds [1–7]. An ion beam with acceleration energy of more than 1 MeV/n deposits its energy to a substrate in a region < 10 nm in diameter (an ion track); the depth of the affected region can be regulated by changing the energy or replacing species of ion particles. When organic polymer films are used as a substrate, the materials around the ion track have been damaged enough to be etched out in alkaline solutions because of scission of the polymer main chains. Thus, 'ion track membranes', which possess cylindrical through-holes with diameter ranging from 10 nm to 1 μm, are easily prepared by ion beam irradiation followed by etching out of the damaged part of the material [8–13].

There have been many reports of the ion track membranes using poly(ethylene terephthalate) (PET) and polycarbonate (PC) [14–16]. However, the ion track membrane of chemically and thermally stable polyimide was not obtained by alkaline etching because irradiation sensitivity of polymer films is inversely related to their chemical and thermal stability. On the other hand, polyimide is prepared from the corresponding precursor, polyamic acid (PAA), which is soluble to alkaline solution and possesses poor chemical and thermal stability. Therefore, it should be possible to make an ion track membrane with positive hole patterns starting from the precursor PAA films; then it is transformed thermally into the corresponding polyimides. Furthermore, the extent of imidization degree governs solubility of PAA to alkaline solution, and accordingly makes influence on the sensitivity of the films to ion beam irradiation.

When we applied this precursor method to Kapton (a commercial polyimide film), positive hole patterns appeared on the PAA films with 67–83% imidization degree on irradiation with $^{129}Xe^{23+}$ ion beams followed by alkaline etching [17]. However, the contrast of the positive hole

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patterns was not sufficient for the formation of cylindrical through-holes. Indeed, a hemispheric structure (negative image) appeared on the films instead of positive hole patterns when the imidization degree of the film is 89–94%. The other example of the ion track membranes consisted of polyimides is only a Kapton film followed by an oxidative etchant [18–21]. Thus, we report herein the ion beam imaging of the films of three kinds of partially imidized PAAs that possess a sulfonyl group in the main chain using an alkaline etchant because a sulfonyl group in the polymer main chain is known to be highly sensitive to irradiation [22–23].

2. Experimental section

2.1. Materials

Pyromellitic dianhydride (PMDA) and 4,4′-sulfonyldiphthalic dianhydride (DSDA) were purchased from Tokyo Chemical Industry Co. Ltd, recrystallized from 1,4-dioxane, and dried at 180 °C in vacuo for 10 h. 4,4′-Diaminodiphenyl ether (DDE) and 4,4′-diaminodiphenyl sulfone (DDSO) were purchased from Tokyo Chemical Industry Co. Ltd. 4,4′-Diaminodiphenylmethane (DDM) was purchased from Kanto Chemical Co. Inc., DDE, DDSO, and DDM were recrystallized from ethanol and dried at 60 °C in vacuo for 4 h. *N*-Methyl-2-pyrrolidinone (NMP) was purchased from Tokyo Chemical Industry Co. Ltd, and dried over molecular sieves 4A. 15% Tetramethylammonium hydroxide (TMAH) solution was purchased from Wako Pure Chemical Industry, Ltd.

2.2. Measurement

^{1}H NMR spectra were recorded on a JEOL GSX270W NMR spectrometer in dimethyl sulfoxide d_6 as the solvent and the internal standard. Gel permeation chromatography (GPC) was performed using Shodex KD-804 and KD-805 columns eluted with a mixture of tetrahydrofuran/*N*,*N*-dimethylformamide (50/50, v/v) containing phosphoric acid (0.6 mmol/l) and lithium bromide (0.6 mmol/l) at 40 °C with a flow rate of 1.0 ml/min. Infrared spectra were recorded on a JASCO FT/IR-5300 spectrometer. ATR-IR spectra were recorded using ZnSe crystal on the FT/IR-5300 spectrometer attached with a ATR-500/M. Film thickness was measured using a Mitutoyo SURFTEST SV-600 surface profiler.

2.3. Preparation of PAAs and their partially imidized films

The PAAs were prepared by a condensation reaction between tetracarboxylic acid dianhydrides (TDs) and diamines (DAs) in NMP at room temperature according to a conventional method [24]. The PAAs are described as PAA(TD/DA); these structures are depicted in Fig. 1. The resulting polymer solution was poured into a large amount of water. By this treatment, PAA(PMDA/DDSO), PAA(DSDA/DDE), and PAA(DSDA/DDM) were obtained as white precipitates in yields of 85, 94, and 91%. The number- and weight-average molecular weights of the polymers (M_n and M_w) were determined on the basis of a standard polystyrene calibration as follows: PAA(PMDA/DDSO) (24,000, 34,000), PAA(DSDA/DDE) (44,000, 82,000), and PAA(DSDA/DDM) (27,000, 40,000), respectively. Dimethylformamide solutions of the PAAs (solid content: 25 wt%) were spin-coated on a glass plate ($50 \times 50 \times 1$ mm^3) at 2000 rpm for 30 s. The samples were prebaked at 70 °C for 6 h in vacuo and then heated for 1 h at the prescribed temperatures ranging from 80 to 130 °C. In the case when the imidization temperature was higher than 140 °C, the films were further prebaked at 130 °C for 2 h and then heated at temperatures ranging from 140 to 300 °C for 1 h on an electric hot plate to give partially imidized PAA films with smooth surface.

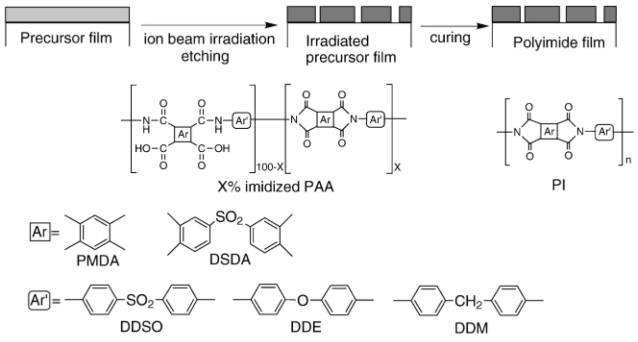


Fig. 1. Schematic illustration of a precursor method for ion beam imaging of polyimide films with the chemical structures.

2.4. Ion beam irradiation and patterning evaluation

Six sheets of film samples were set on the turntable-type film-carrier in a vacuum chamber, which is connected to the azimuthally varying field (AVF) cyclotron on the Takasaki ion accelerators for advanced radiation application (TIARA), Japan Atomic Energy Research Institute (JAERI), Japan. ^{129}Xe^{23+} ion beams with an energy of 3.5 MeV/n were used with fluences of 3×10^7 ions/cm^2. The irradiated films were etched in 0.5, 1, 5, or 15% aqueous TMAH solution at 40 °C without stirring. The specimens were washed with a large amount of water and dried at room temperature. The surface of the films were coated with gold using a Giko IB-3 ion coater and observed with a JEOL JXA-733 scanning electron microscopy (SEM).

3. Results and discussion

3.1. Preparation and determination of the imidization degrees of the partially imidized PAA films

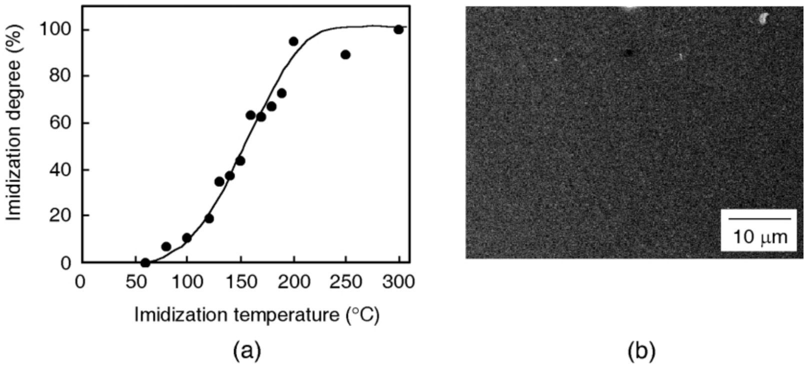
Three polyimide precursors, PAA containing a sulfonyl group in a DA moiety (PMDA/DDSO), PAA containing a sulfonyl group in TD (DSDA/DDE), and PAA containing a sulfonyl group in TD along with a methylene group in DA (DSDA/DDM), were chosen to investigate the relation between structures of the PAA and ion track formation nature against ion beam irradiation. These polymers synthesized were cast on glass plates to prepare the films with thickness of ca. 10 μm (see Section 2). Since the dissolution rates of PAA films reached a constant value for heating interval longer than 1 h, the imidization degrees of the partially imidized PAA were regulated by changing the imidization temperature for the fixed heating time of 1 h. ATR-IR analysis was applied to determine imidization degree for precursor polymer films because these films are too thick to be subjected to a conventional FT-IR analysis due to their strong IR absorbance. The imidization degrees of all the films were successfully calculated using the peak intensity at 1380 cm^{-1}, assigned to absorbance of the imide ring (C–N), against the intensity of the standard peak at 1500 cm^{-1}, as described in a previous paper [17,25].

3.2. Imaging of partially imidized PAA films containing a sulfonyl group

PAA(PMDA/DDSO) films with the imidization degrees ranging from 0 to 100% were prepared by partial imidization at prescribed temperatures ranging from 60 to 300 °C, as shown in Fig. 2(a). When these films were irradiated with $^{129}Xe^{23+}$ ions followed by etching in 0.5 or 1% aqueous TMAH solution, no discernible image was observed on the film surface according to SEM photographs (Fig. 2(b)).

The imidization degrees of PAA(DSDA/DDE) films were successfully regulated vary from 0 to 100% by prescribing the imidization temperatures ranging from 60 to 300 °C (Fig. 3(a)). Etching of the films with 71–91% imidization degrees in a 5% aqueous TMAH solution at 40 °C resulted in no pattern formation on these films, whereas a hole pattern was observed on the same films treated with a thicker TMAH solution (15%) at 40 °C for 10–20 min. The most contrasty hole pattern with 3.0 μm diameter appeared on the 71% imidized film with etching at 40 °C for 20 min, as shown in Fig. 3(b). During the etching, the films thickness decreases to 69% of the original film thickness (3.9 μm) due to the small difference of the dissolution rates between the original film and the damaged area of the irradiated film. The hole density on the film was $7.5 \times 10^5\ cm^{-2}$, which was only 2.5% of the accumulated ion fluence (3.0×10^7 ions/cm^2). The lower hole density of the hole pattern than the accumulated ion fluence implies that the patterns should be formed only at the region where two or more ion tracks overlapped, as was observed in the negative pattern formation of Kapton precursor films [17]. Accordingly, the damage of PAA(DSDA/DDE) induced by single $^{129}Xe^{23+}$ ion particle is not sufficient for the formation of a positive hole pattern.

Fig. 4(a) shows the plot of imidization degree of PAA(DSDA/DDM) against curing temperature. As is the case of PAA(DSDA/DDE) irradiated film treated with a diluted (5 or 10%) aqueous TMAH solution, no hole patterns were observed on films over the any range of imidization degree, while hole patterns were observed on the film with 68–89% imidization degrees by treatment of a 15% aqueous TMAH solution. In particular, the sharpest hole patterns with 0.3 μm diameter were obtained in 89% imidized film, as shown in Fig. 4(b). Since the sharpest hole pattern formation of the film requires a longer etching period (5.5 h) in a 15% aqueous TMAH solution at 40 °C, the films thickness decreases to 80% of the original film thickness (2.6 μm) after the etching. The density of the hole pattern was $3.2 \times 10^7\ cm^{-2}$, which is in good agreement with the accumulated ion fluence of 3.0×10^7 ions/cm^2. This accordance clearly shows that single $^{129}Xe^{23+}$ ion induces enough damage on PAA(DSDA/DDM) films for the formation of a positive hole pattern even though the structure of PAA(DSDA/DDM) is quite similar to that of PAA(DSDA/DDE). The film of the partially imidized PAA(DSDA/DDM) with the hole patterns was transformed to the corresponding polyimide film with curing at 350 °C for 1 h. As can be seen in Fig. 5, the shape of hole patterns



(a)

(b)

Fig. 2. (a) Imidization degrees of PAA(PMDA/DDSO) for the preparation of the partially imidized films as a function of imidization temperatures. (b) The SEM photograph of the surface of the 95% imidized film after $^{129}Xe^{23+}$ ion irradiation with fluence of 3×10^7 ions/cm^2 followed by etching in a 1% aqueous TMAH solution at 40 °C for 5 h.

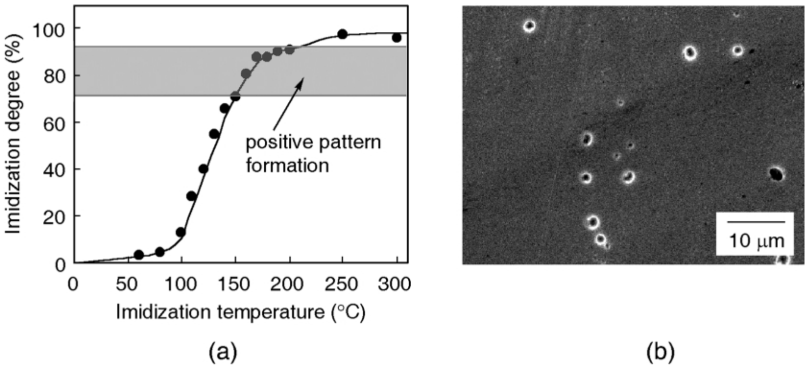


Fig. 3. (a) Imidization degrees of PAA(DSDA/DDE) for the preparation of the partially imidized films as a function of imidization temperatures. (b) The SEM photograph of the surface of the 71% imidized film after $^{129}Xe^{23+}$ ion irradiation with fluence of 3×10^7 ions/cm^2 followed by etching in a 15% aqueous TMAH solution at 40 °C for 20 min.

on the etched film was maintained with enlargement of the pore size during imidization to some extent.

The dissolution rates of partially imidized PAA(DSDA/DDM) films in a 15% aqueous TMAH solution at 40 °C are plotted as a function of the imidization degrees in Fig. 6. The dissolution rates are considered one of the most important factors for the imaging formation of a film. The positive patterns were formed on the 68–89% imidized PAA films, where the dissolution rates were in the range from 0.002 to 0.1 μm/min. The 89% imidized PAA film, on which clear hole patterns were observed, showed the dissolution rate of 0.016 μm/min. These dissolution rates for the positive pattern formation of PAA(DSDA/DDM) are similar to those for Kapton precursor films. The positive patterns were observed with the dissolution rates ranging from 0.010 to 1.0 μm/min, and the most contrasty pattern was attained on the conditions of dissolution rate with 0.050 μm/min. Accordingly, in order to create hole patterns on a polyimide film with sharp contrast, the dissolution rates of the corresponding PAA film should be regulated to be lower than 0.1 μm/min by partial imidization.

3.3. Mechanism of positive pattern formation induced by ion beams

Table 1 summarizes the main chain structures of the PAA, together with the pore density and diameter appeared on the corresponding films irradiated with $^{129}Xe^{23+}$ ion beam followed by alkaline etching in an aqueous TMAH solution. The following key points are concluded from the comparison of the data in Table 1: (1) a sulfonyl group in either DA or TD moiety is not sufficient for increasing the sensitivity of partially imidized PAA films to the extent that single $^{129}Xe^{23+}$ ion particle gives a positive hole pattern on ion track membranes, and (2) a positive hole pattern appeared on the irradiated films made of PAA(DSDA/DDM) containing sulfonyl and methylene groups in TD and DA moieties, respectively. Thus, it is obvious that both sulfonyl and methylene groups are necessary for the ion beam-induced degradation of the PAA main chains, which results in the positive hole pattern formation on the films. On the other hand, it is not easy to understand why the ion beam sensitivity of PAA(DSDA/DDE) containing a sulfonyl group in a TD moiety is somewhat higher than that of PAA(PMDA/DDSO) containing a sulfonyl group in a DA

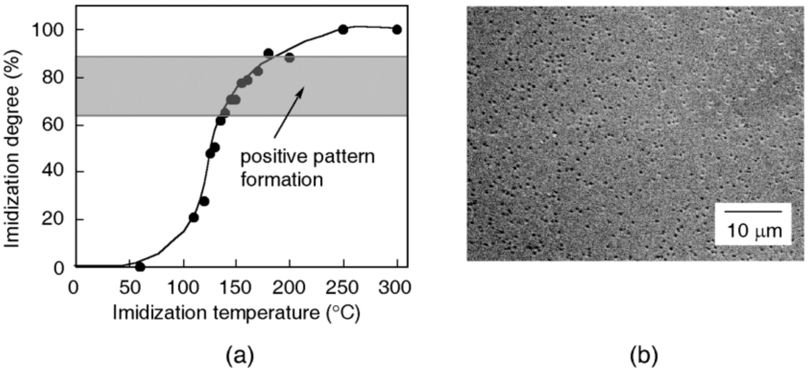


Fig. 4. (a) Imidization degrees of PAA(DSDA/DDM) for the preparation of the partially imidized films as a function of imidization temperatures. (b) The SEM photograph of the surface of the 89% imidized film after $^{129}Xe^{23+}$ ion irradiation with fluence of 3×10^7 ions/cm^2 followed by etching in a 15% aqueous TMAH solution at 40 °C for 5.5 h.

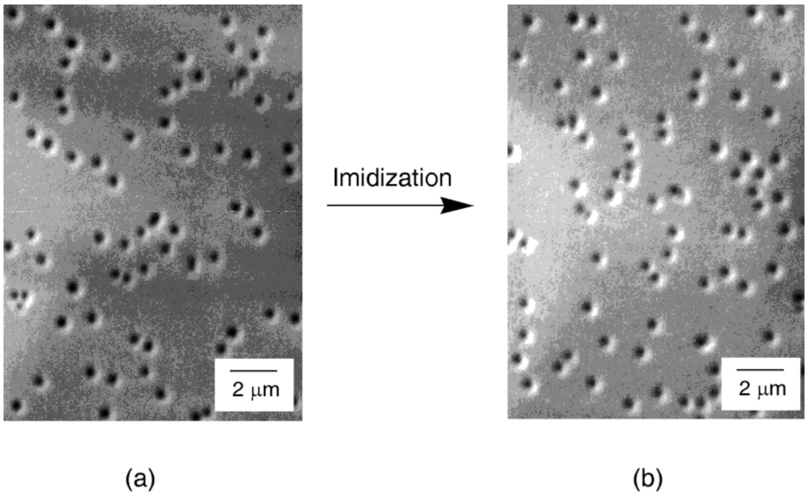


Fig. 5. SEM photographs of (a) the positive image on the 89% imidized PAA(DSDA/DDM) film after $^{129}Xe^{23+}$ ion irradiation followed by etching in a 15% aqueous TMAH solution at 40 °C for 5.5 h and (b) the corresponding polyimide film after curing at 350 °C for 1 h.

moiety. However, it should be explained by the following reason: the ether bond in PAA(DSDA/DDE) should be susceptible to ion beams, whereas PAA(PMDA/DDSO) containing pyromellitic acid structure in TD moiety is less soluble to an alkaline etchant due to its rigidity, resulting in no appearance of a positive hole pattern at the damaged area in the irradiated film.

From the structural comparison of the polymers, we suggested the possible mechanism for degradation of PAA, as shown in Fig. 7. First, the C–S bond cleavage should readily takes place to generate two radicals (sulfonyl and aryl radicals) since it is well known that polymers containing sulfonyl group cleave to generate radicals in radiolysis. The generated radicals will then recombine with each other to revert to the original polymer, assuming that there is no radical source such as hydrogen radical in the polymers consisted of only aromatic amide and acid in PAA(PMDA/DDSO) and PAA(DSDA/DDE). In contrast, the sulfonyl radicals generated in PAA(DSDA/DDM) films could abstract hydrogen radicals from the methylene groups of the polymer, resulting in the cleavage of the main chain for degradation. Furthermore, the benzyl radicals derived from the methylene group presumably induce further chain reactions such as cleavage and radical abstraction, resulting in degradation of the polymers.

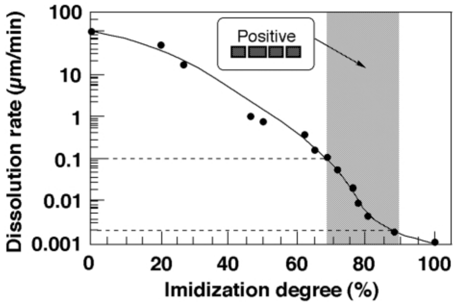


Fig. 6. The plots of the dissolution rates of the PAA(DSDA/DDM) films in a 15% aqueous TMAH solution at 40 °C as a function of the imidization degrees of the films.

4. Conclusion

No discernible pattern was observed on the films of partially imidized PAA(PMDA/DDSO) and PAA(DSDA/DDE), which contains a sulfonyl group, over the whole range of imidization degrees. In contrast, positive hole patterns appeared on the films of the partially imidized PAA(DSDA/DDM), which contains both sulfonyl and methylene groups, with 68–89% imidization degrees. The most contrasty hole patterns with 0.3 μm diameter were achieved on the PAA films of 89% imidization degree. The irradiated film with the hole patterns was then transformed to the corresponding polyimide film with curing at 350 °C for 1 h. The structural comparison of the polymers implies that the positive pattern formation requires both sulfonyl and methylene groups in the main chain. The former should cleave to generate radical pairs and the latter should act as a radical source of the chain reactions for polymer degradation.

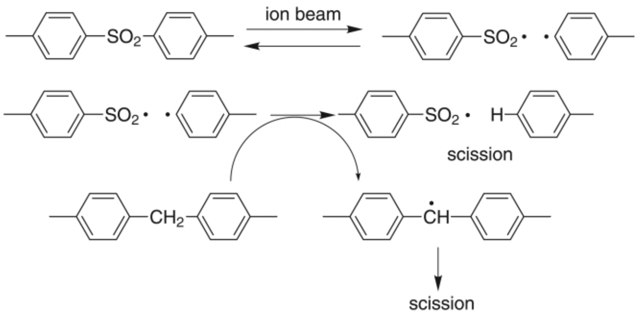
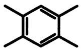
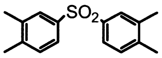
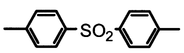
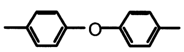
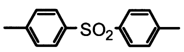
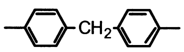


Fig. 7. The proposed mechanism for degradation of partially imidized PAA by irradiation with ion beams.

Table 1

The structures of tetracarboxylic acid dianhydrides (TDs) and diamines (DAs) in polyamic acids (PAAs), along with pore density and diameter appeared on these films by $^{129}Xe^{23+}$ ion beam radiation followed by alkaline etching in an aqueous TMAH solution

Polymer	TD	DA	Pore density (pores/cm^2)	Pore diameter (μm)
PMDA/DDSO			–	–
DSDA/DDE			7.5×10^5	3
DSDA/DDM			3.2×10^7	0.3

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