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A STUDY OF THE ION BEAM GRAFT POLYMERIZATION METHOD

—observation of graft chains in grafted polymers—

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ABSTRACT

Graft polymerization method is one of the most effective methods to produce a new polymer which has a unique function. To produce the polymer, we have conducted experiments on radiation graft polymerization with several hundred-keV ion beams. After a high density polyethylene (PE) film was irradiated with H^+ beams, graft polymerization with monomer solution such as acrylic acid was conducted. Radicals generated by interaction between the beam ions and PE molecules become the start point of graft polymerization. Because a range in PE depends on ion energy, density distribution of graft chain can be controlled by ion energy. Using a mask with a thickness smaller than the ion range, PE sheets which contain graft chains only in the unmasked area were obtained. Multiple ion beam graft polymerization can produce a polymer which has some functional bases at specified position. We evaluated both the vertical and the lateral distributions of the graft chain in the sample with a microscope.

Keywords: ion beam, graft polymerization, functional device, adsorbent

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1. INTRODUCTION

We find many kinds of industrial products made of graft polymers everywhere; for example, a deodorizer, a paper diaper, and so on. The graft polymerization method is one of the most effective methods to produce a new polymer, and the polymer can be produced with a property of base polymer and additional property of grafted polymer. The additional property is supplied by functional bases in the grafted polymer chains. For example, a polymer which has a hydrophilic property can be fabricated by introducing hydrophilic base. Among many kinds of functions, an adsorption is one of the most useful functions in our life. Adsorbent which can recover rare metals dissolved in environmental water is an example of the graft polymer with the adsorption function. An amidoxime (AO) adsorbent with amidoxime functional groups is a candidate for recovery of rare metals, such as uranium and vanadium, from sea water (Tamada *et al.* 2004). The AO adsorbent can also recover harmful substance in environmental water (Shiraishi *et al.* 2003). Another example is polymer brushes produced by surface-initiated living radical polymerization (Tsujii *et al.* 2006).

The graft polymers are produced using radiation frequently and effectively. Generally, electron beams are utilized for this method. When polymer is irradiated by radiation, secondary electrons (δ-rays) are generated by ionization of molecule in polymer, then a radical generation, bond cleavage between two atoms, and cross-linking between polymer chains occur, and hydrogen atoms are released from the polymer (Taniike *et al.* 2002). Radicals which are generated by polymer irradiation can be used for the original point of grafting in graft polymerization.

In our laboratory, we demonstrated a radiation graft polymerization method with ion beams (IBGP) (Kitamura *et al.* 2004). Because ions have large LET compared with electrons at the same energy, stopping range of the ions at 1 MeV, for example, in a polymer substrate is as small as several ten μm. When a substrate is irradiated with the ion beam, radicals are generated in the near-surface region around the range. After graft polymerization graft chains are then expected to be localized in the near-surface region. Final goal of our study is to arrange specified functional bases at specified position in a polymer three-dimensionally with multiple ion beam graft polymerization method (multiple IBGP) proposed in the previous work (Taniike *et al.* 2011). An example of the procedure is shown in Figure 1. Two different graft chain regions are produced in the depth direction by multiple IBGP with monomer A and B. Graft chains can be also localized in the surface direction with masking method. Using this method, a functional polymer device such as a semi-conductor device can be produced.

In this paper properties of IBGP method mentioned below are reported. The first subject is to control the depth distribution of the graft chains. After graft polymerization the grafted PE expands corresponding to the degree of grafting. We observed the phenomenon with a microscope, and considered influence of the expansion to produce functional polymer. The second is to control the lateral distribution of the graft chains. We compared a size of the opening in a mask with the

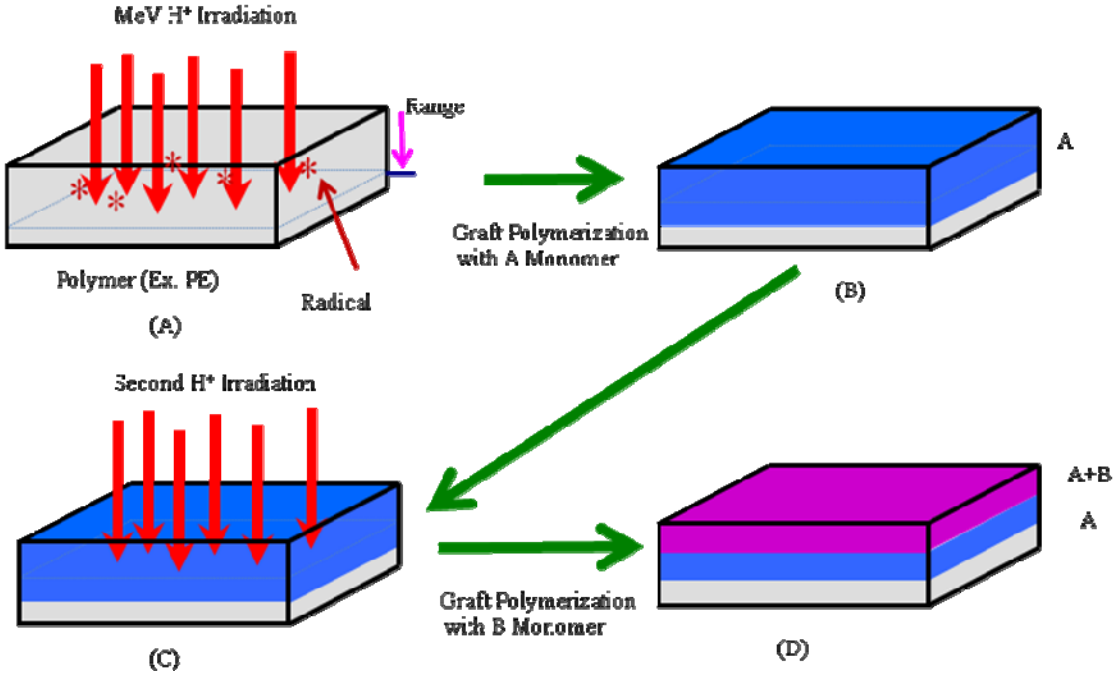

Figure 1 Procedure of multiple ion beam graft polymerization,; the first irradiation (A), graft polymerization with A monomer solution (B), the second irradiation (C), and graft polymerization with B monomer solution (D).

size of the grafted area.

2. EXPERIMENTS

2.1 Production of Ion Beams

Polymer films are irradiated with H^+ ion beams generated by a tandem accelerator at Kobe University (Pelletron, model 5SDH-2, NEC). The accelerator can generate the H^+ ion beam whose energy is varied from 200 keV to 3.4 MeV. Polyethylene (PE) films are used as substrates where IBGP is developed in this work. The range of H^+ in PE depends on energy, and the stopping power dependence on depth from the PE surface. The range, the longitudinal straggling, and the lateral straggling can be calculated by SRIM2008 and the stopping power was calculated by our code based on Ziegler (1985). The results of these calculations are shown in Table 1 and Figure 2. Because a thickness of PE sheet used in our experiments was 50 μm, 2.0 MeV-H^+ ion can penetrate the PE. There is no Bragg peak in that case.

Table 1 Range of H^+ ions in PE and straggling for some incident energies. Stopping power at the PE surface is also listed.

Energy [keV]	Range [μm]	Longitudinal Straggling [μm]	Lateral Straggling [μm]	Stopping Power [keV/μm]
200	2.3	0.1	0.1	74
400	5.7	0.2	0.2	49
600	10.5	0.4	0.4	37
1000	23.4	1.0	0.7	27
1500	44.8	1.8	1.3	21
2000	71.8	2.8	1.9	17

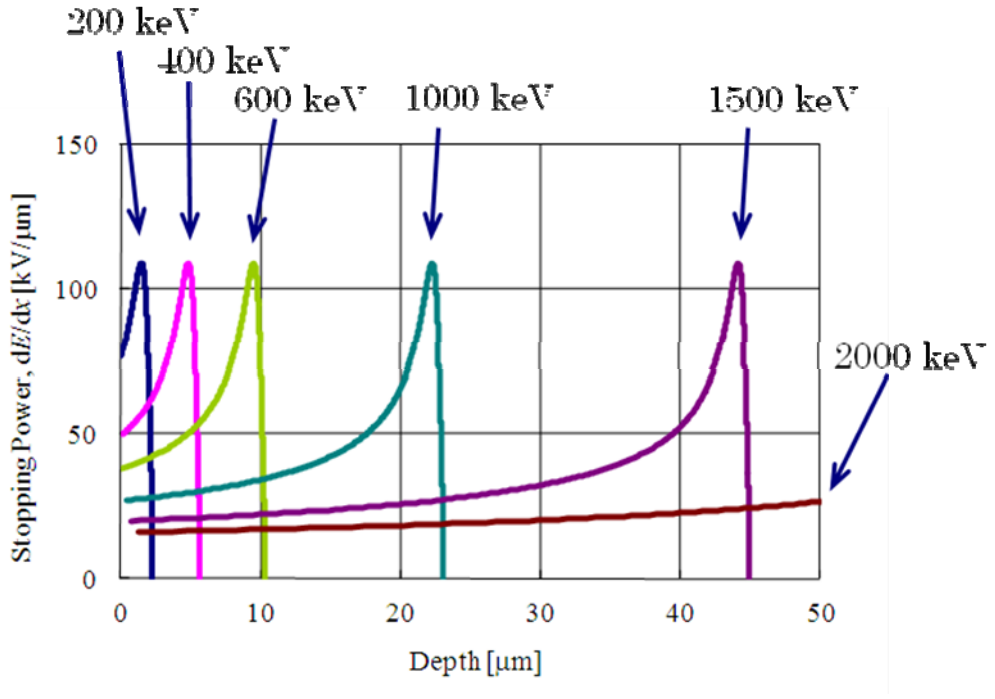

Figure 2 Stopping power of H^+ ions in PE for some incident energies.

2.2 Irradiation

The beam irradiation was made with a rotary sample holder shown in Figure 3. It is located in a vacuum chamber, and the pressure is typically in the order of 10^{-4} Pa. The diameter of the holder is 110 mm and the width is 50 mm, and the holder rotates at a speed of 2.4 rpm. Using this mechanics a long polymer sheet can be irradiated at once. Six PE pieces (30 mm × 50 mm × (50 ± 1) μm) are set usually on the holder, and a small PE piece (15 mm × 35mm) is also set for regulation of beam shape. The holder

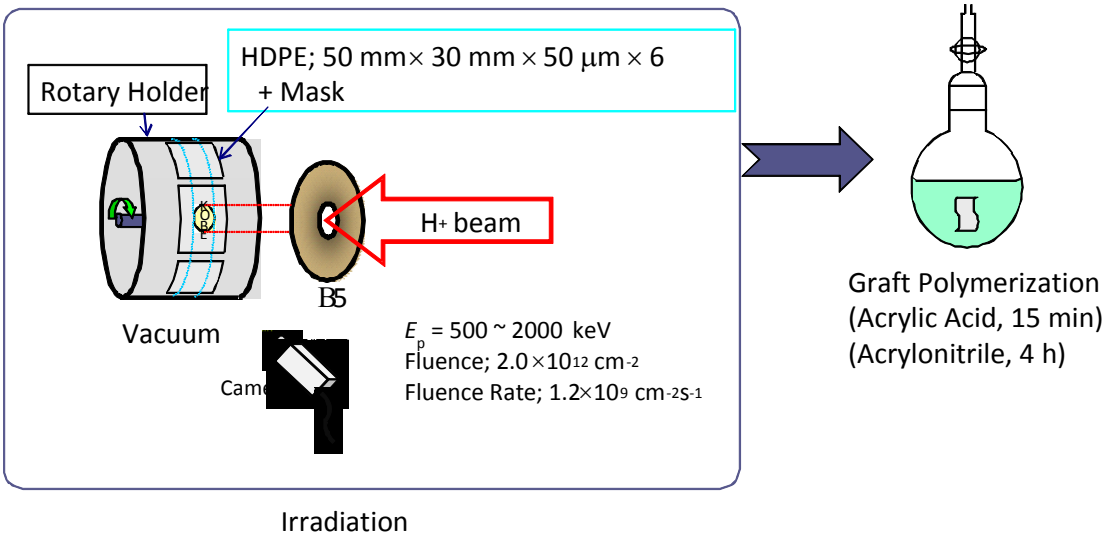

Figure 3 Experimental set up for PE irradiation by ion beams.

can be biased at +270 V to suppress secondary electrons. A video camera is installed outside the chamber, and bright luminescence under beam incidence can be monitored. Observing the image we adjust beam optics of the accelerator to make spatially uniform beams.

2.3 Graft Polymerization

Since heavy ions produce a too large irradiation effect in a substrate, it is difficult to use in the IBGP method. Therefore H^+ ion beams have been used, whose energy is 200 -3400 keV. The beam parameters for typical irradiation are the following; the fluence is 2.0×10^{12} cm^{-2}, the fluence rate is 1.2×10^9 $cm^{-2}s^{-1}$. Degree of grafting has dependence on the fluence and the fluence rate. These parameters were chosen so as to give the optimized irradiation condition. The fluence is equivalent to a dose of several hundred kGy, which is almost the same in graft polymerization with electron beams.

After irradiation, the PE sheets were taken out of the chamber filled with Ar, and inserted into a flask. The flask was immediately evacuated to prevent loss of radicals. Because those monomer solutions include a polymerization inhibitor such as hydroquinone monomethyl ether (HQME), which is active only in the presence of oxygen, bubbling is needed in use to make the MEHQ inactive. The bubbling was made with nitrogen gas for about an hour at 40 °C. A monomer solution was introduced into an evacuated flask.

The monomer used in this study is mainly acrylic acid (AA; CH2:CHCOOH) and acrylonitrile (AN; CH2:CHCN). Other monomers such as Methacrylic acid (MA) and 2-hydroxyethyl methacrylate (HEMA) are also used for copolymerization. The Styrene and Glycidyl Methacrylate (GMA) can also be suitable for graft polymerization. These monomer and other chemicals such as Dimethyle Sulfoxide (DMSO) are made by

Nacalai Tesque, Inc., Japan, and were used as received. These chemical reactions shown in Figure 3 were conducted in a hood. The sample weight was measured with a micro balance which has a precision of ten μg (Mettler Toledo; AX205).

As copper atoms are adsorbed in a sample by functional bases, e.g. the carboxyl base, it can be considered that the copper density distribution in sample represents the density profile of the graft chain.

The degree of grafting, D_G, is expressed by the following equation,

$$D_G\,[\%] = (W_0 - W_1) / W_0 \times 100,$$

where W_0 is the weight of the section of original PE to be exposed to the radiation, and W_1 is the weight after graft polymerization. Since the graft chains propagate in the polymer from original radical only by a few μm at most, the above equation is approximately correct and conveniently used to estimate monomer introduction. The degree of grafting thus calculated involves uncertainty of about 10 % due to systematic errors mainly in the chemical conditions, the irradiation conditions, and so on.

3. RESULTS AND DISCUSSIONS

3.1 Depth Distribution of Graft Chains

Cross sections of the grafted samples mentioned above were observed by a microscope (Syodensya, Model SH200PC). After the sample was fixed by paraffin, the surface was scraped off until the section that we want to observe appeared. An example of the section observed by the microscope is shown in Figure 4. The sample was prepared with multiple IBGP method. In the first irradiation whole PE was irradiated with 1.0 MeV H^+ ion beam, and in the second irradiation right side of PE was irradiated with 1.5 MeV H^+ ion beam. In other word, the right side was irradiated with both 1.5 MeV H^+ and 1.0 MeV H^+ ion beam. AA monomer solution was used in both graft polymerization reactions. After the procedure the sample was immersed in $Cu(NO_3)_2$ solution, and the region that includes graft chains was colored blue. The width of left side part is 91μm and the width of right side is 39μm. Those widths are corresponding with the range of ion.

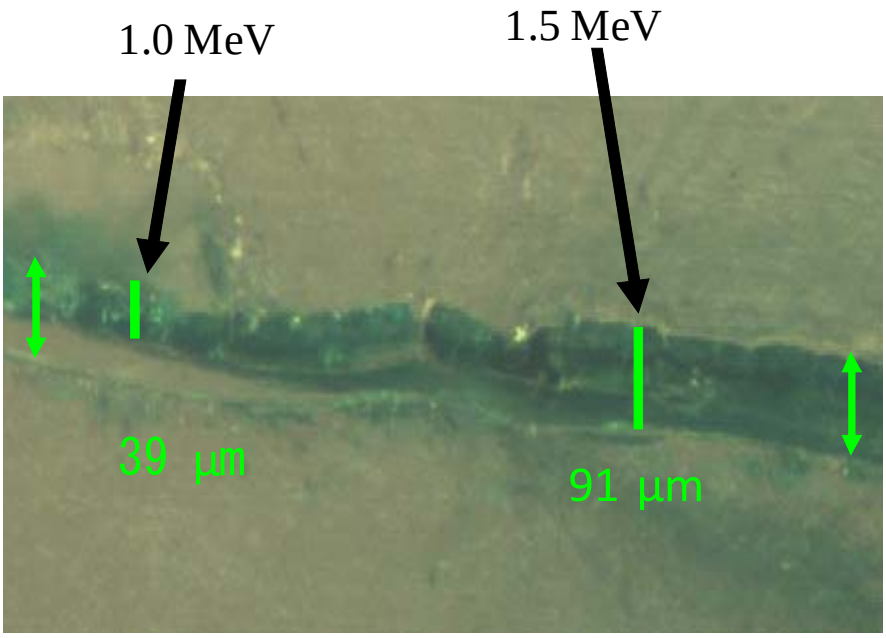

Figure 4 Cross sectional view of a sample made with multiple ion beam graft polymerization method.

Otherwise the range of 1.0 MeV H^+ ion in PE is 23.8 μm, and the width of grafted part at the left side is 38.8 μm. The reason is sample swelling in graft polymerization reaction. Similarly, the width of grafted part at the right side is thicker than original width of 50 μm. Relationship between the degree of grafting and the thickness of grafted part. The thickness is normalized by original PE thickness, and the normalized thickness is expressed in R_{GP}. Calculated thickness corresponding to the degree of grafting is also shown in Figure 5. In this calculation we assumed that the density of poly acrylic acid (PAA) is 1.18 g/cm^{-3}. The experimental value is larger than calculated value. This is because actual density of PAA is a little smaller than the calculated value. Because PAA chains are propagated in PE chains and the chains produce a gap in polymer, it is considered that actual density is decreased. There is same dependence for ions in some energy. To produce a functional element in precisely, the swelling by graft polymerization must be taken into account.

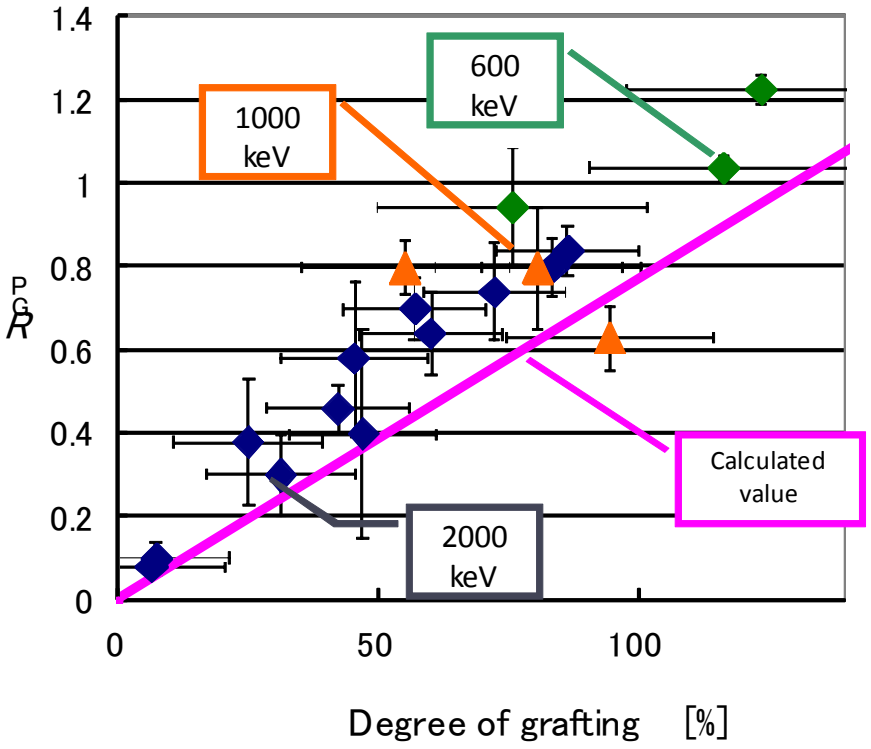

Figure 5 Normalized thickness of grafted part as a function of degree of grafting. The calculated one is also shown.

3.2 Lateral Distribution of Graft Chains

In this section we discuss the difference between size of mask and size of grafted part. A hole was drilled in mask material, and the radius is smaller than a few hundred micro meters. Using a mask made of aluminum with some small holes, IBGP was conducted using ion beams with energies of 1.0 MeV. Then the grafted PE was observed by the microscope. Relationship between the radius of the hole and the grafted area is shown in Figure 6. The experimental data was fitted well by a linier equation. The gradient is 1.00 and the intercept is 11±1 μm. The grafted area is larger by 11 μm independently on the radius of hole. The dependence is shown in Figure 7 for the ion energy of 1.0 MeV and 1.4 MeV. It is found that the dependences of the data for both ion energies are effectively the same.

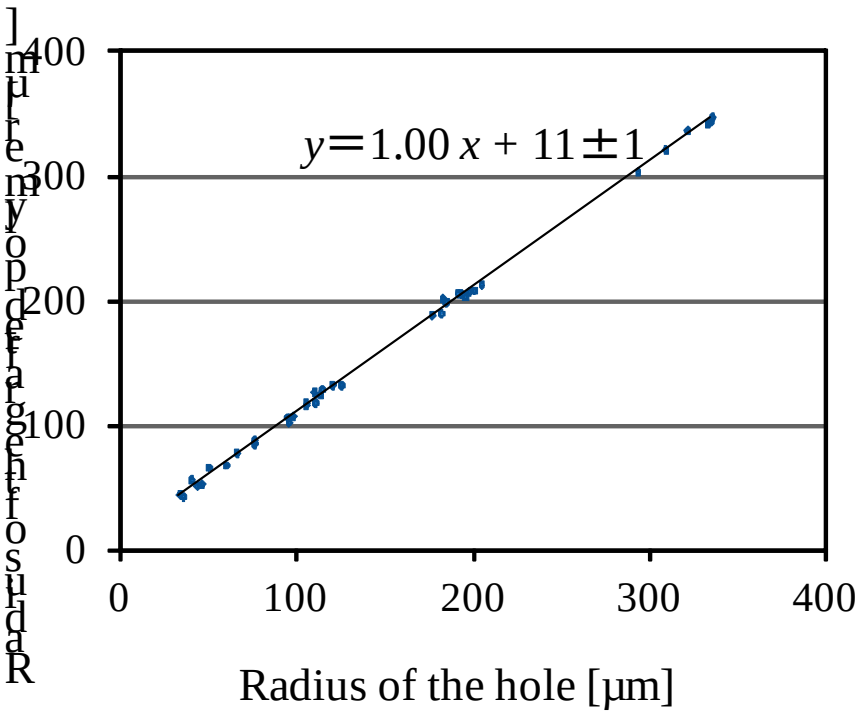

Figure 6 Relationship between the radius of the grafted area on the PE and that of the corresponding hole in the mask. A linear fitting is also shown as a line.

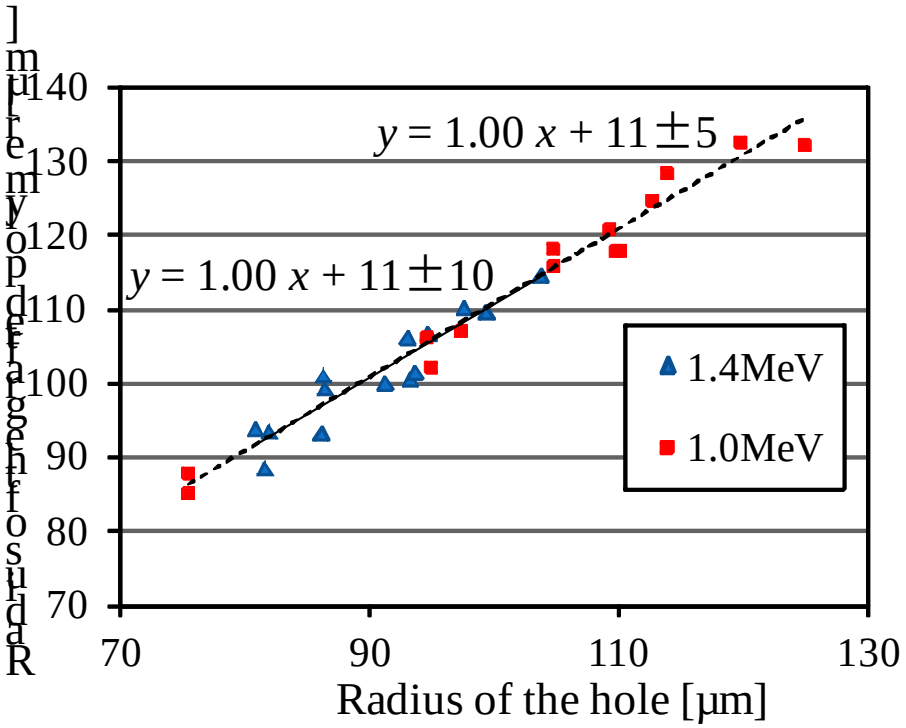

Figure 7 Relationship between the radius of the grafted area on the PE and that of the corresponding hole in the mask. The ion energies are 1.4 MeV and 1.0 MeV.

The reason why there is the intercept is discussed. Some candidates are presented in the following;

(1) There might have been thin regions around the holes in the Al foil mask. Ions could have penetrated the thin potions of the mask, and could have been incident on PE.

(2) Because of finite emittance of the beam penetrating the mask and/or the PE, the beam could have irradiated the PE with an area larger than the holes.

(3) Radicals generated by irradiation could have moved out of the irradiated region.

(4) Graft chains could have propagated to outside region.

(5) Swelling could have occurred in graft polymerization as described in section 3.1.

The intercept, i.e. the expansion of grafting area, could be caused by all candidates above. Here, the absolute value of the effect (4) is estimated as follows. Supposing that the graft chain consists of 10000 monomer units and the scale of a monomer is 0.1 nm, the length of the chain is estimated to be roughly 1 μm. Because contribution of each candidate is considered to be less than several μm, the value, 11 μm, seems to be somewhat large. The expansion of the grafting area gives a practical limitation on the size of a possible functional device. Therefore, to develop a smaller device, it is necessary to clarify the expansion mechanism in detail.

4. SUMMARY

In the present paper properties of IBGP method were reported. In addition to conventional analysis of the grafted samples, observation of the samples with microscope was conducted. The discussion was focused on two subjects. The first subject was to control the depth distribution of the graft chains. The second is to control that in the lateral direction. We obtained some important information on production of a functional device with multiple IBGP method.

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