INTRODUCTION PROCESS OF *N*-METHYLGLUCAMINO GROUPS FOR BINDING ANTIMONY(III) TO A POLYMER BRUSH

Tomonori SAITO[1], Hidetaka KAWAKITA[1], Kazuya UEZU[2]*,
Satoshi TSUNEDA[3], Masao TAMADA[4]

[1] Advanced Research Institute for Science and Engineering,
Waseda University, 2-2 Hibikino, Kitakyushu 808-0135, Japan
[2] Department of Chemical Processes and Environments,
The University of Kitakyushu, 1-1 Hibikino, Kitakyushu 808-0135, Japan
e-mail: uezu@env.kitakyu-u.ac.jp
[3] Department of Chemical Engineering, Waseda University, 3-4-1 Ohkubo,
Shinjuku, Tokyo 169-8555, Japan
[4] Takasaki Radiation Chemistry Research Establishment,
Japan Atomic Energy Research Institute, 1233 Watanuki, Takasaki,
Gunma 370-1292, Japan

ABSTRACT

Polymer brushes containing epoxy groups were grafted onto a porous hollow-fiber membrane by radiation-induced graft polymerization of glycidyl methacrylate. *N*-Methylglucamino (NMG) groups for binding antimony(III) were introduced to the epoxy groups of the polymer brush using a range of reaction times. To determine the process of the introduction of NMG groups to the polymer brush, the water permeability through the membrane, the swelling ratio of the membrane, and the antimony(III) adsorptivity of the membrane were determined for different NMG conversion values of 0 - 76%. The water permeability and the swelling ratio indicated that the NMG groups reacted with the epoxy groups of the polymer brush on the outside of the base of the polymer first, and then with those inside the base of the polymer matrix. The molar ratio between the NMG groups and the antimony(III) adsorbed on the polymer brush was always 0.5, demonstrating that the NMG groups were introduced from the tail end of the polymer brush to the fixed end due to diffusion and reaction of the NMG groups along the polymer brush.

* Corresponding author

INTRODUCTION

Antimony(III) oxide (Sb_2O_3) has been used in many applications as a clarificant, pigment, flame retardant, and catalyst [1]. Antimony(III) is contained in wastewater from these processes [2]. For example, in polyester production antimony trioxide is used as a homogeneous catalyst for polymerization, and small quantities of this catalyst are contained in effluent from these plants. The LD_{50} for antimony, the measure of its toxicity, is 100 mg/kg in rats [3]. WHO guidelines state that antimony levels in drinking water should be no more than 0.005 mg/L [4]. This means that removal of antimony from contaminated wastewater is necessary.

Many researchers developed antimony(III) adsorbents. Antimony(III) was separated mainly by adsorbents with trimethylbenzylammonium [5], sulfonic acid [6], or methylamino glucitol [7] functional groups. Deorkar and Tavlarides [8] prepared silica gel ceramics with pyrogallol group at the density of 0.26 mmol/g and succeeded in adsorbing 43 g-Sb(III)/kg in a column. There is a need for more efficient adsorbents to recover antimony(III) from contaminated wastewater.

We have so far proposed permeation-aided removal of antimony (III) using chelating porous hollow-fiber membranes prepared by radiation-induced graft polymerization (RIGP) [9,10]. Epoxy groups of the poly-glycidyl methacrylate brush were converted into polyol ligands [11-13], namely, 2,2-iminodiethanol, 3-amino-1,2-propanediol (APD), and *N*-methylglucamine (NMG) groups. Of these, the NMG-ligand-containing porous hollow-fiber membrane had the highest binding capacity for antimony(III). The NMG groups introduced on the polymer brush formed a complex with antimony(III) at the ratio of 2:1 in experimental and computational approaches [13]. Antimony(III) coordinated two polyol ligands on the polymer brush, thus, the configuration of polyol ligands governs the binding performance of antimony(III). Therefore, to take advantage of the structural characteristics of the polymer brush and to develop a high performance antimony(III) separation material, it is very important to introduce the ligands at the appropriate position on the polymer brush.

The molecular weight of the attached polymer brush and the site at which NMG is introduced to the polymer brush strongly influence the antimony (III) adsorption. For example, the length and density of the functional polymer brush will determine the permeability of the liquid and the adsorptivity of the molecules. However, because the membrane made of polyethylene has high mechanical and chemical strength, it is very difficult to evaluate the polymer brush by tearing it off the membrane. In this study, the process of the introduction of NMG groups to the polymer brush grafted onto a porous hollow-fiber membrane by RIGP was indirectly investigated, by examining: (1) water permeability through the membrane, (2) swelling phenomena, and (3) antimony (III) adsorption by the membrane.

EXPERIMENTAL
Reagents

A commercially available porous hollow-fiber membrane made of polyethylene, supplied by Asahi Kasei Corporation (Japan), had inner and outer diameters of 1.9 and 3.1 mm, respectively, with a pore diameter of 360 nm and porosity of 70%. It was used as the trunk polymer for grafting. Glycidyl methacrylate (GMA, $CH_2=CCH_3COOCH_2CHOCH_2$) and *N*-methylglucamine (NMG, $CH_3NHCH_2(HCOH)_4CH_2OH$) were purchased from Tokyo Kasei and Wako Pure Chemical Industries, respectively. Other chemicals were of analytical grade or higher.

Antimony(III) oxide (Sb_2O_3, Wako Pure Chemical Industries) was dissolved in 1 M sodium hydroxide to yield 100 mg-Sb/L antimony(III) solution. The pH of the 10 mg-Sb/L Sb_2O_3 solution was adjusted to 11.4 with sulfuric acid.

Preparation of porous hollow-fiber membranes containing NMG ligands

Preparation of the porous hollow-fiber membranes containing NMG ligands involved three steps, as shown in Fig. 1: (1) irradiation with an electron beam using a cascade-type accelerator to produce radicals throughout the trunk polymer, (2) grafting of an epoxy-containing monomer, GMA, onto the electron-beam-irradiated trunk polymer, and (3) introduction of NMG, the $-NCH_3CH_2(HCOH)_4CH_2OH$ (NMG) group into the epoxy group of the poly-GMA chain. Details of these procedures were described in our previous publication [13]. Grafting and subsequent functionalization were expressed by the degree of grafting and the molar conversion of the epoxy group to the NMG, as follows:

$$\text{degree of grafting (\%)} = 100 \text{ (mass of poly-GMA chain)} / \text{ (mass of trunk polymer)} \quad (1)$$

$$\text{molar conversion (\%)} = 100 \text{ (moles of polyol ligand introduced)} / \text{ (moles of epoxy group before functionalization)} \quad (2)$$

The degree of GMA grafting was set at 160%. The GMA-grafted and the NMG-ligand-containing hollow fiber are referred to as GMA and NMG(x) fibers, respectively. The x in parentheses denotes molar conversion.
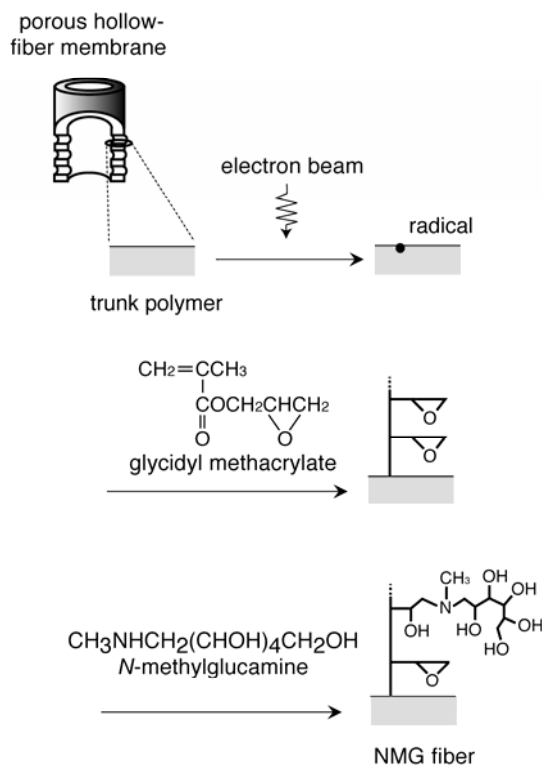
Fig. 1. Reaction scheme for the introduction of NMG groups to a polymer brush attached to a porous hollow-fiber membrane.

Properties of the membrane

The flux of water at pH 11.4 was determined at the constant permeation pressure of 0.1 MPa at 298 K. The flow rate of water penetrating the outside of the fiber was determined, and then converted to the water flux as follows:

flux (m/h) = (permeation rate)
/ [(inner surface area of the fiber) (permeation time)]   (3)

The inner and outer diameters and the length of the membrane were measured with a scale. The swelling ratio was determined using the following equation:

swelling ratio (-) = (membrane thickness after funtionalization)
/ (membrane thickness before functionalization)   (4)

11

Permeation of antimony(III) solution through NMG fiber

The antimony(III) oxide solution (10 mg of Sb/L, pH 11.5) as a feed was forced to permeate radially outward from the inside surface of the hollow-fiber membrane with an effective length of 2.0 cm to the outside surface at the constant permeation rate, 80 mL/h, using a pump. The effluent at the outside surface of the hollow-fiber membrane was continuously sampled and its antimony concentration was determined by ICP-AES (Perkin Elmer, OPTIMA 4300 DV CYCLON) at the Instrumentation Center, University of Kitakyushu.

The equilibrium binding capacity of the fiber for antimony(III) was evaluated by the following integration:

$$\text{equilibrium binding capacity (mg/g)} = \int_0^{V_e} (C_0 - C)dV / W \qquad (5)$$

where C_0 and C are antimony(III) concentrations in the feed and effluent, respectively. W is the mass of the hollow-fiber membrane. V and V_e are the effluent volume and the effluent volume when C reaches C_0, respectively. The amount of antimony bound onto the fiber was expressed as the binding ratio:

$$\text{molar ratio (-)} = \text{(equilibrium binding capacity of Sb(III))}$$
$$/ \text{(NMG density in polymer brush)} \qquad (6)$$

RESULTS AND DISCUSSION
Properties of the membrane

Differing amounts of NMG groups were introduced to the polyGMA brush by changing the reaction times, with 76% molar conversion being achieved after 2 hours of reaction followed by equilibration. The swelling ratio and the water flux at different NMG molar conversion values are shown in Fig. 2. With increasing molar conversion, the flux first decreased drastically, and then increased gradually. The swelling ratio was constant up to the molar conversion value of 40 %, and then increased gradually, reaching the membrane thickness 1.1 times that of the GMA fiber at maximum.

Polyethylene has amorphous and crystalline domains. Radiation creates radicals throughout the trunk polymer. The radicals created in the amorphous domain immediately disappear by contacting with oxygen in the air, while the radicals in the crystalline domain remain due to lack of oxygen contact [14]. The radicals created in the crystalline domain play the crucial role in the RIGP; the grafting monomer diffuses through the amorphous domain and reacts with the radicals migrating from the inside to the surface of the crystalline domain. The grafted polymer grows in the

amorphous domain as well as outside the trunk polymer. Therefore, the polymer brush is present both inside and outside the membrane (Fig. 3).
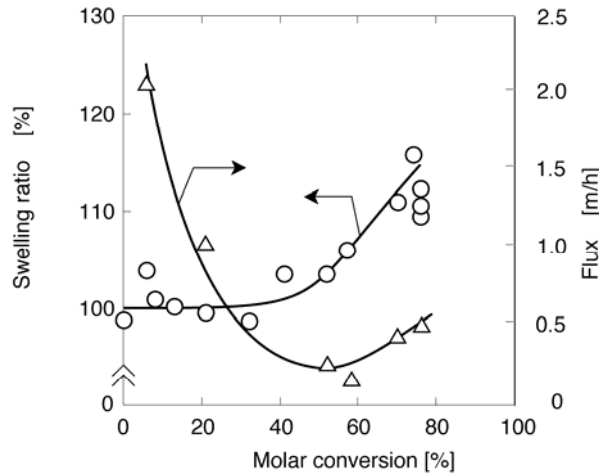
Fig. 2. Swelling ratio and flux of the NMG fiber as a function of molar conversion.
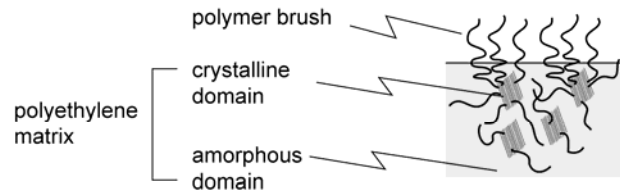
Fig. 3. Illustration of the polymer brush grown from the matrix.

The swelling of the membrane results from the introduction of NMG groups inside the amorphous domain of the polymer matrix. The beginning of the swelling process at the molar conversion below 40% indicates that NMG groups are introduced to the polymer brush outside the polymer matrix first, and then on the inside of the matrix.

The water permeability through the membrane relates to the extension and shrinkage of the polymer brush. Initially, the introduction of more NMG groups lowered the permeability due to the pore diameter decrease resulting from the polymer brush extension. At higher NMG molar conversion values, however, the swelling of the matrix induced a certain degree of increase in the pore size, which increased the permeability.

13

Change in pore radius resulting from NMG introduction

The introduction of NMG groups to the membrane induced the extension of the polymer brush and the swelling of the amorphous domain in the matrix. To determine the change in pore diameter quantitatively, the Hagen-Poiseuille equation was applied to the above phenomena with the assumption that the pore was cylindrical throughout the membrane [15].

The fluxes of water through the GMA fiber F_0 and the NMG fiber F are described as follows:

$$F_0 = n_0 \pi r_0^4 \Delta P / 8\mu D_{T0} \tag{7}$$

$$F = n\pi r^4 \Delta P / 8\mu D_T \tag{8}$$

Hence:

$$F/F_0 = (n/n_0)\, (r/r_0)^4\, (D_T/D_{T0}) \tag{9}$$

where n, r, and D_T are: the number of pores per unit of the inside surface area, mean pore radius, and thickness of the membrane, respectively; μ and ΔP are the liquid viscosity, and the pressure difference across the membrane. Assuming that the total number of pores is constant, one can write that:

$$n_0\, d_0\, L_0 = n\, d\, L \tag{10}$$

where d and L are the inner diameter and the length of the membrane. The dimensionless pore radius, i.e. the pore radius defined as the ratio of the pore radius of the NMG fiber to that of the GMA, was calculated from eq. (11):

$$r/r_0 = [(F/F_0)\, (d/d_0)\, (L/L_0)\, (D_T/D_{T0})]^{1/4} \tag{11}$$

The dimensionless pore radius, r/r_0, is shown in Fig. 4. the value of r/r_0 gradually decreased down to 0.6 with an increase in the molar conversion up to 40% and then increased again to 0.8. The changes in the matrix and the polymer brush are summarized in Fig. 5. Initially, NMG groups were introduced to the polymer brush outside the matrix, inducing the extension of the brush and decreasing the pore diameter (Fig. 5 (b)). With the increasing molar conversion, NMG groups were introduced to the brush inside the matrix, swelling the membrane and thus increasing the pore diameter (Fig. 5 (c)).
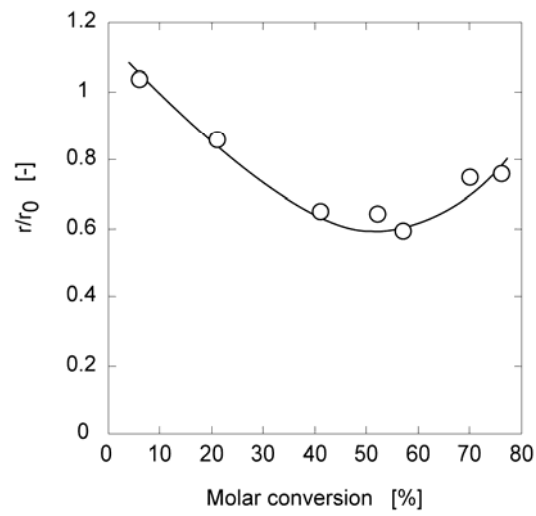
14

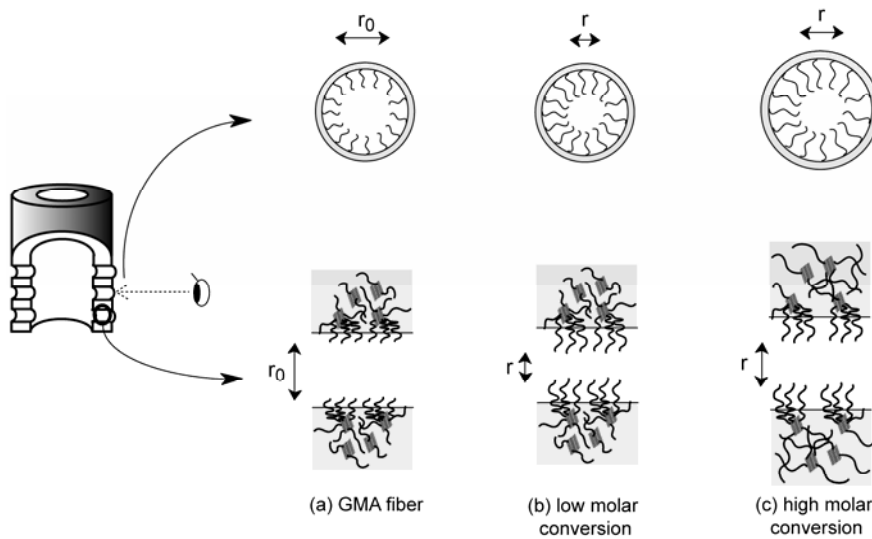Fig. 4. Pore radius ratio vs molar conversion.

Fig. 5. Illustration of the structure of the polymer brush at low and high molar
conversions to NMG groups.

**Introduction process of NMG groups to the polymer brush as
determined by antimony(III) binding**

Antimony(III) was adsorbed to NMG fibers on the polymer brush
with different NMG molar conversion values in order to understand the

introduction process of NMG groups to the polymer brush more thoroughly. The equilibrium binding capacity and molar ratio, calculated from eq. (5) and (6), against the molar conversion are shown in Fig. 6. The equilibrium binding capacity was gradually increased with increasing molar conversion, and the maximum antimony(III) binding capacity was 110 mg/g at 76% molar conversion. However, the molar ratio of NMG to antimony(III) was 0.5 irrespectively of the molar conversion. This indicates that all the NMG groups on the polymer brush always take part in antimony(III) binding because two NMG groups on the polymer brush form a complex with one antimony(III) [13].
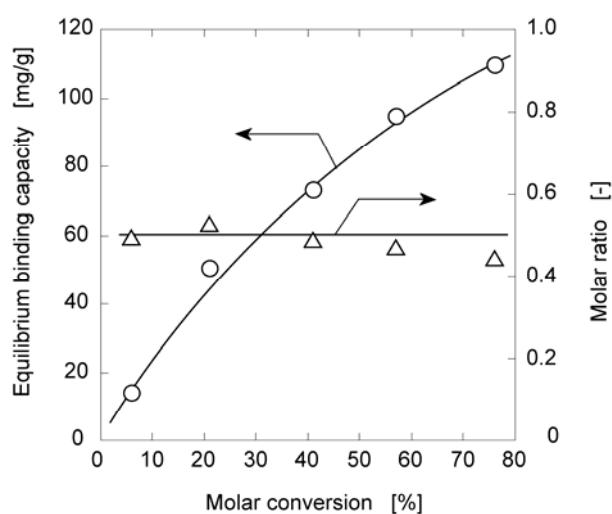

Fig. 6. Effect of molar conversion on the equilibrium binding capacity and molar ratio.

Water permeability and the swelling ratio of the membrane revealed that NMG groups were initially introduced to the polymer brush on the outside of the matrix, and then to that on the inside. Moreover, the molar ratio of 0.5 that was obtained irrespectively of the molar conversion shows that NMG groups are introduced from the tail end of the polymer brush to the fixed end, so that two adjacent NMG groups form a complex with antimony(III) due to the diffusion and reaction of the NMG groups along the polymer brush.

CONCLUSIONS
Using radiation-induced graft polymerization of glycidyl metha-crylate, an epoxy-group-containing polymer brush was grafted onto a porous hollow-fiber membrane. NMG groups that form a complex with antimony(III) were introduced to the epoxy groups of the polymer brush with differing reaction times. The introduction of NMG group to the

16

polymer brush was considered to be important for the efficient binding of antimony(III). To recognize the process by which NMG groups are introduced to the epoxy groups, the permeability of water through the membrane, the swelling ratio of the membrane, and the adsorption of antimony(III) were evaluated over a range of NMG molar conversion values. The results indicate that the NMG groups are introduced to the epoxy groups at the tail end of the polymer brush outside the polymer matrix first, and then to the epoxy groups in the matrix. This understanding of the NMG introduction process could enable the design of high-performance separation materials based on a grafted porous hollow-fiber membrane taking into account the polymer brush morphology and the functional group arrangement.

REFERENCES

[1]   K.L. Herbst, G. Rose, K. Hanusch, *Ullmann's Encyclopedia of Industrial Chemistry*, vol. A3, fifth ed., VCH, Weinheim, 1985, pp. 55-76.

[2]   K. Ando, N. Tsuchida, *JOM*, 1997, 49-51.

[3]   S. Gangolli, *The Dictionary of Substances and Their Effects*, Second ed., The Royal Society of Chemistry, Cambridge, UK, 1999, pp. 332-335.

[4]   *Guidelines for Drinking-Water Quality*, vol. 2, second ed., World Health Organization, 1996, pp. 940-949.

[5]   R. Guin, S.K. Das, S.K. Saha, *J. Radioanal. Nucl.Chem.*, 1998, *230*, 269-271.

[6]   F. Nelson, D.C. Michelson, *J. Chromatogr.*, 1996, *25*, 414-441.

[7]   U. Schilde, H. Kraudelt, E. Ullmann, *React. Polym.*, 1994, *22*, 101-106.

[8]   N.V. Deorkar, L.L. Tavlarides, *Hydrometallurgy*, 1997, *46*, 121-135.

[9]   H. Yamagishi, K. Saito, S. Furusaki, T. Sugo, *Ind. Eng. Chem. Res.*, 1991, *30*, 2234-2237.

[10] S. Konishi, K. Saito, S. Furusaki, T. Sugo, *Ind. Eng. Chem. Res.*, 1991, *31*, 2722-2727.

[11] S. Nishiyama, K. Saito, K. Saito, K. Sugita, K. Sato, M. Akiba, T. Saito, S. Tsuneda, A. Hirata, M. Tamada, T. Sugo, *J. Membr. Sci.*, 2003, *214*, 275-281.

[12] T. Saito, S. Tsuneda, A. Hirata, S. Nishiyama, K. Saito, K. Saito, K. Sugita, K. Uezu, M. Tamada, T. Sugo, *Sep. Sci. Technol.*, 2004, *39*, 3011-3022.

[13] T. Saito, H. Kawakita, K. Uezu, S. Tsuneda, A. Hirata, K. Saito, M. Tamada, T. Sugo, *J. Membr. Sci.*, 2004, *236*, 65-71.

[14] K. Uezu, K. Saito, S. Furusaki, T. Sugo, I. Ishigaki, *Radiat. Phys. Chem.*, 1992, *40*, 31-36.

[15] S. Tsuneda, H. Kagawa, K. Saito, T. Sugo, *J. Colloid Interface Sci.*, 1995, *176*, 95-100.