O-B1

Polyamide-imide Torlon as Membrane Materials

Masakazu Yoshikawa[a], Ako Higuchi[a], Michael D. Guiver[b], Gilles P. Robertson[b]

[a] Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Kyoto 606-8585, Japan
Phone, +81-75-724-7816; Fax, +81-75-724-7800; e-mail, masahiro@ipc.kit.ac.jp

[b] Institute for Chemical Process and Environmental Technology, National Research Council of Canada, Ottawa, Ont., Canada K1A 0R6
Phone, +1-613-993-9753; Fax, +1-613-991-2384; e-mail, michael.guiver@nrc-cnrc.gc.ca

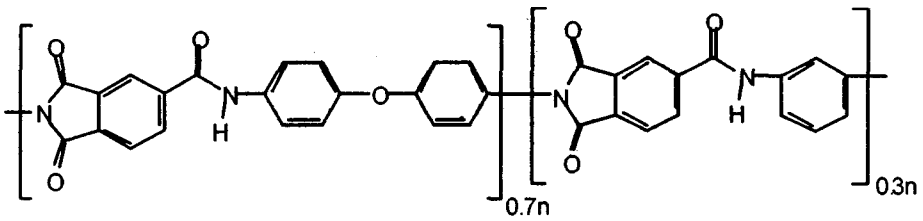
Keywords: Adenosine; 9-Ethyladenine; Guanosine; Molecular Imprinting; Molecular Recognition; Optical Resolution; Polyamide-imide; Surface Plasmon Resonance (SPR), Torlon® 4000T

1. Introduction

Molecular imprinting, which was first proposed by Wulff and Sarhan in 1972 [1], is a facile way to construct molecular recognition sites by applying a simple radical polymerization [2]. Since 1994, the authors have proposed an alternative molecular imprinting method in which polymeric materials are directly converted into molecular recognition materials [3]. By applying this, polymeric materials such as oligopeptide derivatives, natural polymer derivatives, and synthetic polymers [3] were converted into molecular recognition materials, membranes, and sensors. Our attention was focused on molecularly imprinted materials from synthetic polymers. There are many commercial available synthetic polymers, which have the potential to be converted into molecular recognition materials by applying an alternative molecular imprinting, among which is Torlon 4000T. Torlon 4000T is a polyamide-imide utilized for various applications in industrial processes, transportation, electrical equipment and so on since it shows superior mechanical thermal, and oxidative properties. Torlon 4000T is comprised of amide and imide structural groups within the polymer and those functional moieties are expected to play an important roles in molecular recognition *via* hydrogen bonding. From this, Torlon 4000T was adopted as a candidate polymer forming molecular recognition sites. Their recognition ability was studied by using surface plasmon resonance (SPR) spectroscopy. In the present study, the nucleic acid component adenosine was adopted as a model target molecule in connection with biosensors, drug therapy, genetic engineering, and so forth. To this end, recognition sites towards adenine were constructed by adopting 9-ethyladenine (9-EA) as a print molecule. The recognition of adenosine/guanosine (As/Gs) was studied as a model mixture.

2. Experimental

Torlon® 4000T polymer was obtained from BP Amoco Polymers Inc. (now Solvay Advanced Polymers). The chemical structure of Torlon® 4000T, which was required in order to determine the molar ratio of imprint molecules to the constitutional repeating unit of the polymer, was previously determined by ^{1}H and ^{13}C NMR spectroscopy and published information in the scientific literature [4].



The film was prepared by spin casting a 1.0 g dm^{-3} DMF solution of Torlon polyamide-imide onto a pre-treated gold-deposited glass plate. The rotation speed was 5000 rpm. A prescribed amount of the print molecule 9-EA was dissolved in the spincasting DMF solution for the preparation of molecularly imprinted films. 9-EA was omitted for the preparation of control films.

The molecular recognition of the prepared films toward the target molecule As was evaluated by SPR spectroscopy. The change in incident angle ($\Delta\theta$) responding to the addition of substrate was recorded on the SPR apparatus (SPR670S, Nippon Laser & Electronics Laboratory).

3. Results and Discussion

Fig. 1 shows the adsorption isotherms of As and Gs on the control non-imprinted film. $\Delta\theta$ cannot be directly converted into the concentration of a given substrate adsorbed in the spin-cast film, even though the value of $\Delta\theta$ is proportional to the amount of the adsorbed substrate. Both apparent adsorption isotherms of As and Gs are superimposed and not distinguishable. Also, both adsorption isotherms are straight lines passing through the origin, implying As and Gs were non-specifically adsorbed in non-imprinted Torlon.

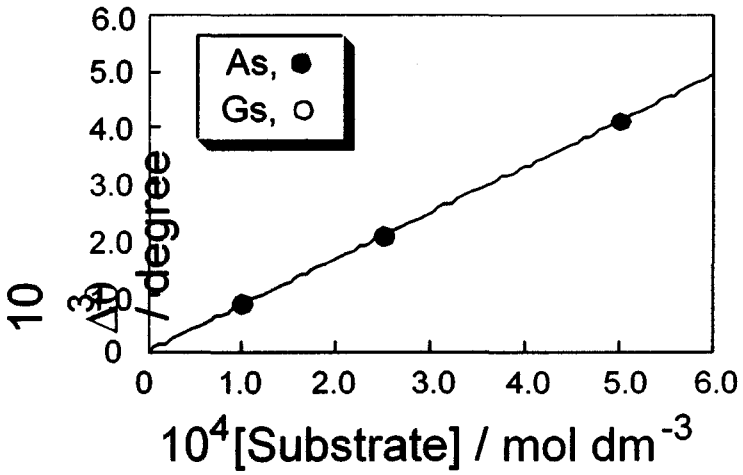


Fig. 1 Adsorption isotherms of As and Gs on the control non-imprinted Torlon film.
(The two curves of As and Gs are superimposed and not distinguishable.)

The apparent adsorption isotherms for 9-EA imprinted Torlon are shown in Fig. 2. In the figure, the molecular imprinting condition, the molar ratio of the amount of 9-EA to that of constitutional repeating unit of Torlon® 4000T was 0.10. The molecular imprinted films, of which molecular imprinting conditions were 0.20 and 0.30, were also studied. Those molecularly imprinted films gave similar adsorption isotherms like that shown in Fig. 2. The adsorption isotherm of Gs in Fig. 2 is a straight line passing through the origin like that for non-imprinted film shown in Fig. 1. This led to the conclusion that there is no specific recognition site toward Gs in 9-EA imprinted Torlon film.

In contrast to this, dual adsorption isotherm was observed for As in 9-EA imprinted Torlon® 4000T, consisting of non-specific adsorption and an adsorption on an As specific recognition site, like dual adsorption of gases [5-7]. The apparent affinity constant between As and the molecular recognition site in the molecularly imprinted films were determined by using the following equation.

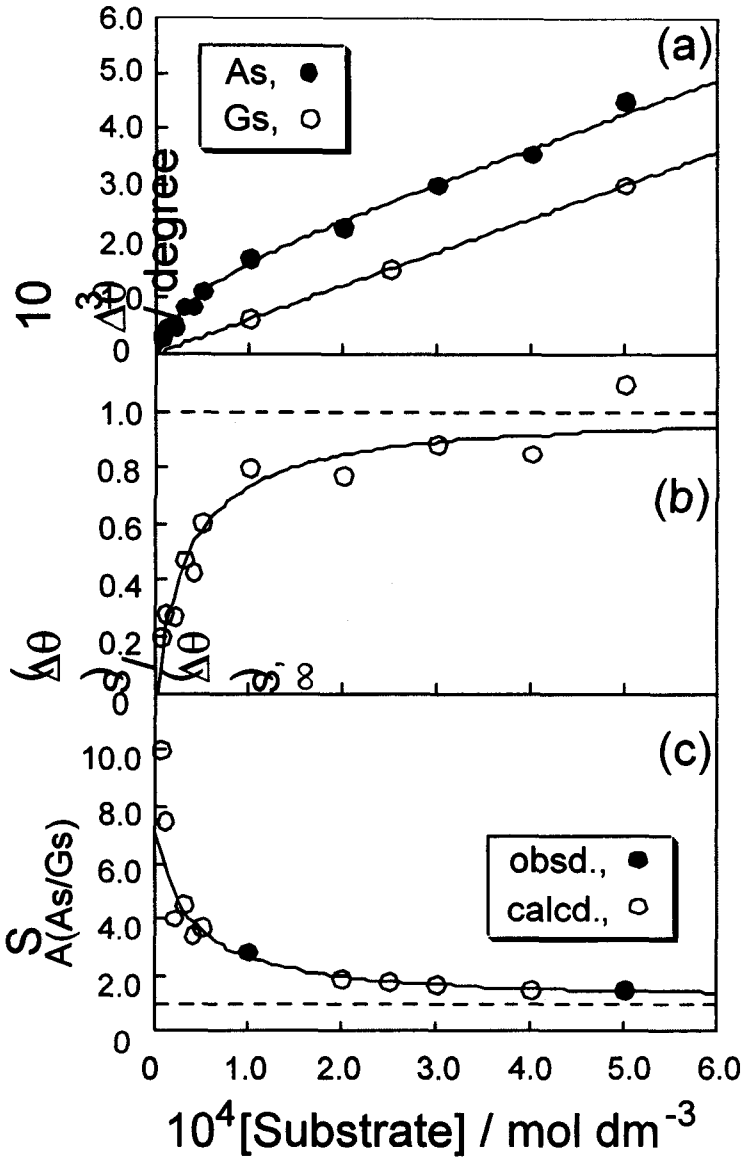


Fig. 2 Adsorption isotherms of As and Gs and adsorption selectivity of the imprinted Torlon film. [(9-EA)/(Torlon) = 0.10]

$$(\Delta\theta)_S/(\Delta\theta)_{S,\infty} = K_{S,app}\,[As] / (1 + K_{S,app}\,[As])$$

where $(\Delta\theta)_S$ is the difference in the shift between that for As and Gs at a given concentration, which corresponds to the apparent amount of As adsorbed on the As recognition site. In the case that there was no experimental $\Delta\theta$ value for Gs at a given concentration, the difference

between the $\Delta\theta$ for As and extended straight line for Gs was adopted as $(\Delta\theta)_S$. $(\Delta\theta)_{S,\infty}$ is the difference in the shift corresponding to the infinite concentration of As. $K_{S,app}$ denotes the apparent affinity constant between As and the molecular recognition site toward As. The apparent affinity constant for the film of the molecular imprinting ratio of 0.10 was determined to be 2.73 x 10^4 $mol^{-1}dm^3$, that for the ratio of 0.20 to be 7.86 x 10^4 $mol^{-1}dm^3$, and that for 0.30 to be 3.80 x 10^4 $mol^{-1}dm^3$, respectively. So far the molecular recognition site toward As was constructed from tetrapeptide derivative, of which sequence was H-Asp(OcHex)-Ile-Asp(OcHex)-Glu(OBzl)-O-CH_2- (DIDE) [8], polysulfone with oligopeptide derivative of glutamyl residues [9], cellulose acetate with 40 % acetyl content [8], and carboxylated polysulfone with a degree of 0.88 [8]. The affinity constants between As and the molecular recognition sites converted from those candidate materials are lower than those three values obtained in the present study. In the molecularly imprinted Torlon films, it can be anticipated that amide and imide moieties play an important role in the recognition of the target molecule, adenosine, *via* hydrogen bonding. Also, the chemical structure of Torlon 4000T polyamide-imide itself is thought to be preferable to discriminate the target molecule with high affinity constant.

4. Conclusions

Novel molecular recognition films were prepared from commercially available Torlon® 4000T polyamide-imide by an alternative molecular imprinting. The molecular recognition films were prepared from Torlon® 4000T by adopting 9-ethyladenine as a print molecule. The molecular recognition sites toward adenosine were constructed in the films thus prepared. The molecular recognition phenomena were studied by SPR spectroscopy. The apparent affinity constant determined by using apparent adsorption isotherms ranged from 2.73 x 10^4 to 7.86 x 10^4 mol^{-1} dm^3. The results obtained in the present study suggests that Torlon® 4000T has comparatively the highest affinity constants we have investigated and thus is one of the most effective candidate materials that has been converted into molecular recognition materials by applying an alternative molecular imprinting.

[1] G. Wulff, A. Sarhan, Angew. Chem., **83**, 364 (1972); G. Wulff, A. Sarhan, Angew. Chem. Int. Ed. Engl., 11, 341 (1972).
[2] G. Wulff, Angew. Cgem. Int. Ed. Engl., **34**, 1812 (1995).
[3] M. Yoshikawa, Bioseparation, **10**, 277 (2002).
[4] G. P. Robertson, M. D. Guiver, M. Yoshikawa, S. Brownstein, Polymer, **45**, 1111 (2004).
[5] W. J. Koros, D. R. Paul, A. A. Rocha, J Polym. Sci., Polym. Phys. Ed., **14**, 687 (1976).
[6] W. R. Vieth, J. M. Howell, J. H. Hsieh, J. Membr. Sci., **1**, 177 (1976).
[7] D. R. Paul, Ber. Bunsenges. Phys. Chem., **83**, 294 (1979).
[8] M. Yoshikawa, J. Izumi, M. D. Guiver, G. P. Robertson, Macromol. Mater. Eng., **286**, 52 (2001).
[9] K. Taniwaki, A. Hyakutake, T. Aoki, M. Yoshikawa, M. D. Guiver, G. P. Robertson, Anal. Chim. Acta, **489**, 191 (2003).